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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

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● VOLUME 2

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for U. S. ATOMIC ENERGY COMMISSION
by ARGONNE NATIONAL LABORATORY

● OCT. 1959

● VOLUME 2

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foreword

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission, Division of Information Services. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are L. Burris, Jr., I. G. Dillon, J. Fischer, A. A. Jonke, S. Lawroski, M. Levenson, W. J. Mecham, W. A. Rodger, W. B. Seefeldt, M. J. Steindler, and V. G. Trice. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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REACTOR FUEL PROCESSING

COMMERCIAL ASPECTS OF FUEL PROCESSING

AEC's Interim Processing Program Meeting

A meeting will be held October 20–21, 1959, at Richland, Washington, to present the AEC's plans (under the Interim Processing Program) for processing irradiated fuels from power, test, and research reactors.

Plans for Processing Power Reactor Fuels at Hanford

Present Hanford plans[1] call for integration of power reactor fuels into existing facilities as follows: receiving and storage, mechanical treatment, and dissolution facilities will be located at the uranium recovery plant; dissolver solution will be piped to the Redox plant for separation and decontamination to uranyl nitrate and plutonium nitrate; conversion of uranyl nitrate to uranium trioxide would be done at the present uranium calcination facility. No further treatment of the plutonium nitrate is contemplated in the present project.

Receiving and storage facilities would provide a cask transfer station so that an incoming cask could be transferred to a captive railroad car. The cask would enter the uranium recovery plant and be unloaded. Fuel elements would be stored in large tanks which could be converted for this purpose. On removal from the canyon, minor decontamination of the cask could be effected if required at the cask transfer station. The mechanical treatment facility would provide for the removal of end fittings, minor disassembly, and size reduction of the fuel elements.

It is anticipated that one dissolver system would be installed initially. Either chopped or whole fuel elements could be charged; since the explosion hazards associated with the leaching of zirconium-clad fuels are not yet defined, clads would be dissolved first by the Zirflex (NH_4F-NH_4NO_3) process and the cores dissolved in a second step. In the case of stainless-steel-clad fuel elements,[1a] the cladding would be removed by the Sulfex process and the cores dissolved in a second step. To ensure compatibility of Zirflex and stainless-steel dissolving media, the dissolver would be constructed of a suitable corrosion-resistant material, presumably Hastelloy F.

The separation and decontamination of the plutonium and uranium will be by solvent extraction, using hexone as the solvent.

AEC and Private Fuel Processing Costs

R. J. Klotzbach of Union Carbide Nuclear Company presented a paper at the 1959 National Industrial Conference Board (NICB) management conference on Uncertainties in Nuclear Fuel Reprocessing Costs, in which he said: "Processing reactor fuel in a one ton per day privately financed multipurpose plant, provided the plant could operate at full capacity, may cost $36,000 per day when the plant realizes a minimum return on the investment for a new venture."[2] Additional data permit the comparison shown in Table I-1 between the derivation of AEC's daily chemical processing charge,[3] based on a one ton per day plant, and a comparable charge on the same size private plant. Klotzbach pointed out that costs for building and operating a privately financed facility would be higher than those for an addition to an existing AEC installation because of the costs of auxiliary service facilities unique to the operation,

Table I-1 COMPARISON OF ESTIMATED FUEL PROCESSING COSTS IN AEC* AND PRIVATE PLANTS

	AEC Plant†	Private Plant
Fixed investment	---	$29,250,000
Working capital	---	750,000
Total investment	$20,570,000	$30,000,000
Annual depreciation at 10%	$2,057,000	$2,925,000
Annual operating and waste storage	1,936,000	2,800,000
Subtotal	$3,993,000	$5,725,000
Annual AEC overhead at 15%	599,000	---
Return on investment before taxes at 17%	---	5,075,000
Total	$4,592,000	$10,800,000
Daily charge (300 days/year)	$ 15,300	$ 36,000

*The numbers are not escalated to 1959 costs.

†Hypothetical multipurpose plant design used to determine AEC fuel processing charge.[3]

i.e., radiochemical laboratories, health physics services, maintenance shops, etc.

Waste Disposal License Review

As the result of exceptions filed by an intervenor, the AEC will review a Hearing Examiner's intermediate decision[4] that a license should be granted a Houston, Texas, firm to collect low-level prepackaged radioactive wastes and to dispose of them in the deep waters of the Gulf of Mexico about 180 miles south of Galveston.[5] A final decision as to issuance of a license to Industrial Waste Disposal Corporation will not be made until the Commission's review has been completed.

Criteria for Ocean Disposal

The National Academy of Sciences–National Research Council panel, which recently recommended 28 sites between Boston, Massachusetts, and Corpus Christi, Texas, for off-shore disposal of packaged, low-level radioactive wastes, has announced the following criteria for safe disposal of these wastes: survey of water circulation and inventory of bottom-living organisms; limitation of wastes to 250 curies per year and 100 curies per month of Sr^{90} or its equivalent, per site; separation of adjacent disposal areas by at least 75 miles and limitation to three areas in any 300-mile coastline; use of "sinkable" containers; and periodic monitoring. Limitations were based on potential return of radioactive wastes to man by ingestion of contaminated marine food products.[6]

ICC Opposes Trucking Embargoes

In June 1959, the Interstate Commerce Commission (ICC) issued a notice which took exception to recent embargoes by trucking companies against shipment of radioactive materials. The cause of the embargoes reportedly is the companies' understanding that insurance is not available to cover liability or damage arising from such shipments. The Mason and Dixon Lines, Inc., of Kingsport, Tennessee, a trucking concern which has long been active in the transportation of materials out of Oak Ridge National Laboratory, had notified various trucking terminals that the company and 24 connecting carriers have placed an embargo against radioactive materials classed as Poison D and requiring Poison, Radioactive Materials label.[6]

The ICC notice said that it "... is the Bureau's view that the reason given is not a valid reason for a carrier refusing to transport shipments covered by its certificate of public convenience and necessity." The notice warned: "Improper embargoes may lead to proceedings brought by the Commission, other carriers, or shippers to revoke a carrier's certificate." The ICC stated that various forms of coverage are now available to motor carriers and that the only type of insurance not now generally available, although it is being considered by insurers, is that for damage by radioactive contamination to cargo accompanying nuclear material shipments.

Value of Industrially Used Radioisotopes

Last spring the AEC engaged the NICB to undertake a study to determine "as accurately as possible the extent to which radioisotopes are being used in American industry and benefits which are resulting from these uses." The NICB survey produced among other things the following points:[2]

1. The total annual net savings "realized by major industries" from using radioisotopes

amount to $39,177,773, which is approximately one-tenth of AEC's 1957 savings estimate.

2. Petroleum refining and related industries report savings of more than $11.5 million, which is nearly twice the next largest savings category for a single industry (chemical and allied products), and represents 30 per cent of the grand total.

3. The industries following next in order, with each realizing more than $2 million in annual savings, are tobacco manufacturers, rubber and miscellaneous products, paper and allied products, and engineering and architectural services.

References

1. V. R. Cooper, Hanford Atomic Products Operation, Mar. 31, 1959. (Unpublished.)

1a. A. M. Platt, Hanford Atomic Products Operation, private communication.

2. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 5, May 1959.

3. *Reactor Fuel Processing*, 1(1): (February 1958).

4. *Reactor Fuel Processing*, 2(3): (July 1959).

5. AEC to Review Houston Waste Disposal Case, AEC Press Release B-102, July 1, 1959.

6. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 7, July 1959.

Development of mechanical and chemical methods for decladding, dissolution, and head-end treatment for a wide variety of fuel types is continuing. Decladding may be accomplished mechanically or chemically; dissolution is performed chemically, the exact treatment depending on the composition of the fuel.

Mechanical Processing

Many of the newer fuels are clad with materials that will not dissolve in nitric acid. Removal or destruction of the clad by mechanical processing will sometimes permit conventional nitric acid dissolution of the fuel material. Three approaches to mechanical processing of power reactor fuels are sawing, shearing, and pulverizing.

Two types of mechanical treatment of power reactor fuel elements are being investigated at Hanford.[1–4] For the removal of end fittings, sawing is the most likely treatment. For size reduction and/or the exposure of fuel material to dissolving media, shearing appears to be the most attractive approach.

Sawing studies have been made using a dry friction blade for cutting Zircaloy tubing.[2] An off-gas filtration system including a rotoclone and a filter assembly was installed to permit studying the particulate generated during the friction cutting operations. The following observations were made:

1. Some burning of small chips and fines occurred in the saw hood. Burning did not propagate along the Zircaloy tube proper.

2. Not all the particulate generated was oxidized or burned. Up to 10 per cent of the material collected in the rotoclone hopper was metallic zirconium.

3. Approximately 45 sq in. of Zircaloy tubing (approximately $^{3}/_{16}$-in.-thick cut) was cut during the test. This represents roughly the cutting required in trimming the "hardware" from 1 ton of power reactor fuel uranium.

Stainless-steel-clad swaged uranium dioxide rods and stainless-steel-clad uranium–10 wt.% molybdenum rods were sheared under water to investigate the mechanical and particulate handling problems associated with these two important types of reactor fuels.[4] Moderate shear forces (25,000 and 9500 lb/sq in. for uranium-molybdenum and uranium dioxide, respectively) and minor end closures (less than 10 per cent) were observed in shearing. As was expected, the uranium-molybdenum cut cleanly with minimum fines generation, whereas up to 30 per cent of the uranium dioxide disintegrated to form a sludge.

At ORNL mechanical processing tests will be made on both irradiated and unirradiated fuel.[5,6] Fuel elements of the Sodium Reactor Experiment (SRE) and Power Reactor Development Company (PRDC) type (stainless-steel-jacketed fuel pins of uranium or uranium alloy bonded with NaK) can be sheared and leached, but they also appear to lend themselves well to dejacketing techniques. Equipment is being designed to remove the inert end hardware, expel the fuel pins from the stainless cladding, clean the fuel free of the bonding, and can the fuel in aluminum containers for chemical processing. Most of the operations will be carried out under an organic liquid blanket.

Fuel assemblies of the Yankee, Organic Moderated Reactor Experiment (OMRE), Commonwealth Edison, Pressurized Water Reactor (PWR), and Rural Cooperative Power Association types consist of bundles of clad fuel elements held together by welding, brazing, or silver soldering using spacing plates or ferrules. The individual fuel elements are uranium oxide or mixed uranium-thorium oxide pins encased in stainless steel or Zircaloy tubing. A dummy Consolidated Edison fuel assembly consisting of 100 stainless-steel tubes with 3-mil wall thickness joined together by 15-mil wall ferrules was disassembled, first into slabs, then into individual tubes, with a simple portable impact wedge driven by a conventional air hammer.[7,8] The bond between ferrules and tubes has a ten-

sile strength of 30,000 psi; the joints were easily broken with the impact wedge.

In core leaching studies,[9-11] unirradiated 0.4-in.-diameter prototype uranium dioxide fuel elements clad with stainless steel were sheared into 0.5-, 1-, 2-, and 2.75-in. lengths. The uranium was leached out completely by batch treatment with 10*M* nitric acid in 30, 45, 60, and 75 min, respectively. In all tests the ratio of the acid volume to the initial weight of uranium dioxide was 2.5 ml/g (150 per cent excess). Simulated Yankee fuel elements were sheared to 0.5-, 1-, 2-, 3-, 4-, and 5-in. lengths and were subsequently leached free of uranium with 173 per cent excess of boiling 10*M* nitric acid.[12] The leaching times, 40 to 240 min, were greater by a factor of 2 than with 150 per cent excess of 10*M* nitric acid.

Studies of mechanical techniques for safely processing the sodium or sodium-potassium alloy (NaK) reservoirs present in some power reactor fuels have continued.[3,4] Tests have included both high-speed friction sawing and hacksaw cutting of NaK-filled capsules in the presence of water. Friction-saw tests were made under an inert-gas blanket. Loadings up to 48 g of NaK (12 g/capsule) were exposed in a single blade pass (24 g maximum instantaneous exposure) with 2-in. maximum water submergence and a helium-purged hood atmosphere containing less than 5 per cent oxygen. The usual dense white cloud of oxide fumes formed in the saw hood, but no fires or explosions occurred. The NaK exposure rate encountered in this test is twice the rate contemplated during production cutting of PRDC fuel rods. Hydrogen was not detected chromatographically in the saw hood after a cut of over 20 g of NaK was made. The detection limit of the chromatograph is 0.2 per cent of hydrogen in helium.

Chemical Dejacketing

Selective chemical dissolution of fuel jackets and structural components is an attractive alternate to mechanical dejacketing or complete dissolution. Fuel cores thus exposed can be dissolved in another (probably less corrosive) reagent in a second step. The principal jacket materials now in use are aluminum, stainless steel, and zirconium or Zircaloy.

Removal of Zirconium and Zircaloy Jackets

For Zircaloy-clad fuel elements having either an oxide core or a uranium-niobium-zirconium alloy core, the Zirflex process, in which 6*M* ammonium fluoride–1*M* ammonium nitrate is used as a dissolving agent, continues to be studied[13,14] at HAPO and ORNL.

For the dissolution of Zircaloy-2 in nitric acid–hydrofluoric acid–aluminum nitrate solutions, the optimum nitric acid concentration, from a corrosion as well as a dissolution rate standpoint, appears to be in the range[4] of 1*M* to 3*M*. In a 2*M* nitric acid–1*M* hydrofluoric acid–1*M* aluminum nitrate solution, Zircaloy-2 dissolution rates decreased from about 15 to 2.5 mils/hr as dissolved zirconium concentration increased from 0*M* to 0.25*M*.

The solubility of uranyl fluoride in ammonium fluoride solutions decreases from 5*M* to 0.0024*M* as the ammonium fluoride concentration increases[16] from 0*M* to 5*M*. Ammonium nitrate is consumed during decladding according to the equation

$$Zr + 6NH_4F + \tfrac{1}{2}NH_4NO_3 \rightarrow (NH_4)_2ZrF_6 + 5NH_3 + \tfrac{3}{2}H_2O$$

Removal of Stainless-steel Jackets

A Sulfex flow sheet for Yankee Atomic Power Reactor (YAPR) fuel was presented in an earlier Review.[17] In a 4-hr decladding test in boiling 6*M* sulfuric acid of a Yankee fuel pin (stainless-steel-clad uranium dioxide pellets) irradiated to 800 Mwd/ton and decayed four months, uranium and plutonium losses were 0.03 and 0.07 per cent,[12] respectively, confirming previous loss data.

Two prototype Yankee fuel pins irradiated to 500 and 775 Mwd/ton, respectively, were declad with 200 per cent excess boiling 6*M* sulfuric acid.[9] The maximum uranium and plutonium losses to the decladding solution, determined in the presence of undissolved stainless-steel end caps, were 0.012 and 0.05 per cent, respectively.

Unirradiated prototype Consolidated Edison pins were dejacketed with 6*M* sulfuric acid with initial rates of 8 to 11 mg/(sq cm)(min).[8] Uranium losses to the dejacketing solution were approximately 0.2 per cent. Addition of 0.25*M* cadmium sulfate and boric acid to sulfuric acid reduced the decladding rates by 20 per cent. In further tests stainless-steel cladding was removed from Consolidated Edison thorium

dioxide–uranium dioxide fuel in 5 hr with boiling 6*M* sulfuric acid; uranium losses increased from about 0.2 per cent with 200 per cent excess acid to 0.3 to 0.4 per cent with 300 per cent excess acid.[7,14] It was found that the type 304L stainless-steel clad of Consolidated Edison fuel was passivated in boiling 6*M* sulfuric acid containing nitric acid at a concentration[9] higher than 0.015*M*. In 3*M* sulfuric acid–0.1*M* nitric acid, passivation did not occur, but the dissolution rate was lower. In 3*M* and 6*M* sulfuric acid containing 0.2*M* nitric acid, the passivation was easily broken by steel wool in contact with the specimen.

Removal of Aluminum Jackets

At the Savannah River Plant (SRP)[15] removal of aluminum jackets from uranium by a boiling aqueous solution of sodium hydroxide and sodium nitrate has been extended to a variety of shapes of elements. The fuel elements are immersed in the dissolver, and the caustic is added at a controlled rate to the boiling sodium nitrate solution. A ratio of at least 1.65 moles of sodium hydroxide in the initial solution to 1 mole of aluminum to be dissolved is required to ensure complete dejacketing and to prevent the precipitation of sodium aluminate complexes. A sodium nitrate concentration of about 20 wt.% is sufficient to suppress hydrogen evolution such that a minimum of air inleakage is required to keep the concentration of hydrogen in the off-gas below the lower explosive limit.

Processing problems arising from the presence of lead as the bonding agent in BORAX-IV fuel were studied.[9] In dissolving the BORAX-IV aluminum-nickel alloy cladding in nitric acid containing mercuric ion as a catalyst, the rates were very low when lead was present unless the mercury concentration was about 0.5*M*. If not removed during decladding, lead seriously limited the uranium and thorium concentrations that could be attained by dissolution of the core in 13*M* nitric acid–0.04*M* sodium fluoride–0.04*M* aluminum nitrate because of the very low solubility of lead nitrate in concentrated nitric acid.

Dissolution

Simultaneous Dissolution of Jacket and Core

1. *Zirconium Fuel Elements.* Two of the more promising methods for dissolution of zirconium-containing fuel elements are the use of aqueous fluoride–nitric acid mixtures and hydrochlorination (Zircex process). A third process proposed involves dissolution in hydrofluoric acid–hydrogen peroxide.

In work at SRP and BNL[18] on dissolution of Enrico Fermi Fast Breeder Reactor fuel pins (zirconium-clad 90 per cent uranium–10 per cent molybdenum alloy), it was found that, to obtain essentially complete dissolution (~99 per cent) of the core, 14 hr of operation using a dissolving reagent of 2.5*M* nitric acid–0.06*M* hydrofluoric acid was required, rather than the 10-hr cycle originally proposed.

In the original Zircex process complete dissolution of the uranium from the hydrochlorination residue in nitric acid was never achieved. Losses ranged from 1 per cent with the Experimental Boiling Water Reactor (EBWR) (low enriched U^{235}) fuel to 6 per cent with the Submarine Thermal Reactor (STR) (highly enriched U^{235}) fuels. In recent tests[9,11] in which both the nitric acid leached and unleached residues were chlorinated at 550 to 600°C with carbon tetrachloride, the uranium loss was 0.01 per cent for both fuels. Secondary advantages of the use of carbon tetrachloride as a final chlorination agent are reduced corrosion and elimination of possible explosions between uranium-zirconium alloys and nitric acid.

A flow sheet suggested for the dissolution of 7 per cent uranium-zirconium-tin alloy in hydrofluoric acid–hydrogen peroxide[7,10] is as follows: A mixture of 34.4*M* hydrofluoric acid–1.7*M* hydrogen peroxide is fed to the dissolver at a controlled rate. In the final solution the fluoride/zirconium mole ratio is 6. All the uranium and tin goes into solution with the zirconium. Fuel pieces having 2.5 per cent uranium in Zircaloy were dissolved homogeneously in hydrofluoric acid by adding hydrogen peroxide to a calculated terminal concentration[19] of 0.0625*M*. The minimum peroxide required for an integral batch dissolution was shown to be between 0.05*M* and 0.0625*M*.

2. *Stainless-steel Fuel Elements.* Methods of dissolution of fuel elements containing stainless steel include dissolution in nitric acid–ammonium bifluoride mixtures (Niflex), in dilute aqua regia (Darex), and in dilute sulfuric acid (Sulfex).

Further studies of the Niflex process have been made at HAPO.[1–4] Niflex dissolution stud-

ies of 304 stainless steel have continued.[2] Increasing the F/S.S. mole ratio from 5 to 5.5 or 6 with 2*M* nitric acid and 2*M* fluoride increased dissolution of the stainless-steel charge to approximately 99.9 per cent in a 4-hr period. Dissolution of the areas in contact with Hastelloy F was generally obtained.

Stainless-steel-clad sintered uranium dioxide pellets ($\frac{1}{2}$ in. in diameter) were declad in 2*M* nitric acid and 1*M* ammonium bifluoride solution with a nominal F/S.S. mole charge ratio of 7. After a 4-hr decladding period, aluminum nitrate and nitric acid were added to make the solution 2.3*M* nitric acid, 0.66*M* aluminum nitrate, 1.33*M* fluoride, and 0.2*M* stainless steel. Dissolution of the uranium dioxide was essentially complete in 8 hr after the additions. At the end of the run 1 per cent of the stainless steel was undissolved. The undissolved uranium still encased in stainless steel was 0.4 per cent of the total uranium charged.

Dissolution of $\frac{1}{2}$-in.-diameter stainless-steel-clad uranium dioxide pellets and $\frac{3}{4}$-in.-diameter stainless-steel-clad uranium rods was completed on 100-lb batches.[3] A fluoride-to-stainless-steel mole charge ratio of 7 to 8 did not give complete dissolution of the stainless-steel cladding which was 96 to 99 per cent dissolved after 4 hr of operation. Approximately 2 wt.% of the uranium core and 3 wt.% of the uranium dioxide core dissolved in the Niflex solution (2*M* HNO_3, 1*M* NH_4HF_2, and 0.4*M* stainless steel) during the 4-hr decladding period. The uranium dioxide dissolved at average rates of 30 to 60 mils per hour when aluminum nitrate was added to complex the fluoride, and the solution was adjusted to 1.5*M* to 2*M* nitric acid. Dissolution of the uranium dioxide cores was 75 to 99 per cent complete in 8 hr, with 1.5*M* and 2*M* nitric acid concentrations, respectively. The final solution of uranium dioxide contained approximately 0.4*M* to 0.5*M* uranium, 4.8*M* NO_3^-, 1*M* aluminum, 1*M* F^-, and 0.2*M* stainless steel. In the metallic uranium dissolution, average rates of 15 to 30 mils per hour were obtained, although the acidity became quite low and an unstable solution formed at concentrations of about 0.94*M* uranium, 0.2*M* H^+, 4.7*M* NO_3^-, 0.16*M* stainless steel, and 1.3*M* aluminum. This "cut" dissolved 53 per cent of the total uranium present.

Studies on the Niflex process have developed the following information:[4]

1. The reaction with 304 stainless steel involves 0.6 mole of nitric acid and 3 moles of hydrofluoric acid per mole of stainless steel in a downdraft dissolver system.
2. Charge ratios, i.e., moles of fluoride per mole of stainless steel, above 5 are required for complete dissolution.
3. Dissolution of 304 stainless steel averages 10 mils per hour during the first hour of dissolution.
4. Approximately 0.1 mole of hydrogen is liberated per mole of stainless steel dissolved. The peak hydrogen evolution rate is 5×10^{-4} lb mole/(hr)(sq ft) of stainless steel.
5. Corrosion of the Hastelloy F containment vessel is severe.

The Darex process has been extensively studied at ORNL (references 6, 8–10, 16, 19) and HAPO.[1–4] Darex is a head-end process for stainless-steel-containing fuels consisting of three steps:

1. Dissolution in dilute nitric–hydrochloric acid.
2. Chloride removal.
3. Feed adjustment for solvent extraction.

The process may be carried out continuously, semicontinuously, or batchwise using nitric acid concentrations from 61 to 95 wt.%. A recent Darex flow sheet is shown in Fig. 1.

Three full-size unirradiated sintered uranium dioxide stainless-steel (APPR) elements dissolved in 2*M* hydrochloric acid–5*M* nitric acid in 1 hr except for the braze metal. The average rate was 28 g/min at a dissolvent rate of 4.3 liters/min.

Heavily oxided unirradiated stainless-steel–uranium plate type fuel assemblies were dissolved in approximately 20 min similarly to unoxidized fuel. Braze metal and oxide scale were only slightly attacked. During dissolution, foam heights of up to 7 ft were attained. Dissolution rates of 275 g/min were measured in dissolvents with the composition range: 3*M* to 4*M* H^+, 1.7*M* to 2.0*M* Cl^-, 1*M* to 2.6*M* NO_3^-, 50 to 75 g of stainless steel per liter, and 5 to 9 g of uranium per liter to which 5*M* nitric acid–2*M* hydrochloric acid was added continuously at 4.2 to 4.5 liters/min.

Results of tests on removal of chloride from APPR-Darex dissolver product made under flow sheet conditions[9,11] indicated that air sparging assists in chloride removal — removal by sparging is complete in >6 hr. The nitric acid con-

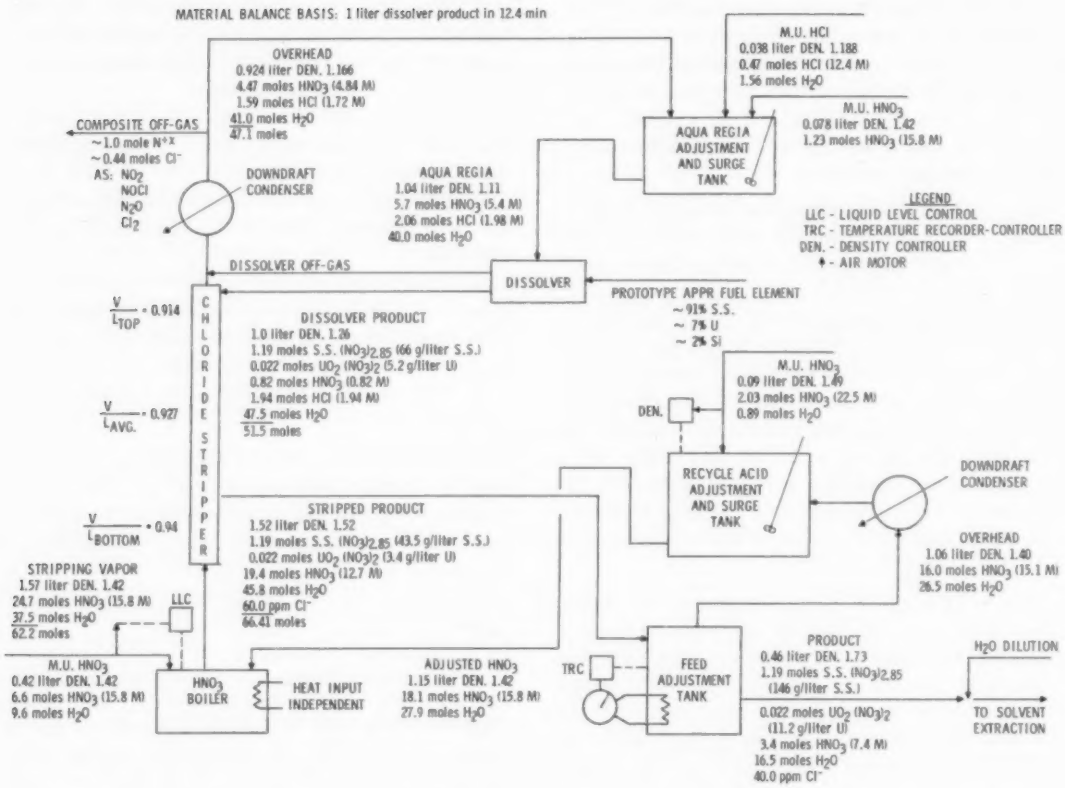

Figure 1 — Continuous Darex process equipment and control flow sheet including material balance.[20]

centration required to remove chloride to 50 ppm, with or without sparging, is >9*M*.

At room temperature, air sparging of a solution of APPR fuel in 5*M* nitric acid–2*M* hydrochloric acid for 12 hr decreased[12,21] the chloride only from 0.65*M* to 0.41*M*. At boiling temperature in 8*M* nitric acid, air sparging decreased the chloride ion concentration to the same extent as nitrogen sparging. Filtration of the chloride-free solution of APPR fuel through bare porous metal appears feasible in a production plant, no difficulty in recovering uranium from the filter cake being anticipated.

Several gelatin and filter aid media were tested[21] for removing silica from dissolver product, prior to chloride removal. The best were 0.004*M* hydrofluoric acid with Celite 545 and 0.004*M* hydrofluoric acid alone; Celite 545 alone, activated alumina, ammonium molybdate, and silica gel were all unsatisfactory. Freezing the solution was also ineffectual. Centrifugation in a 5-in.-diameter solid-blown centrifuge at 3000 rpm completely removed siliceous material at centrifugate flow rates up to 400 cc/min.

Consolidated Edison fuel samples (stainless-steel-clad thorium dioxide–uranium dioxide) were declad with 4*M* nitric acid–2*M* hydrochloric acid with 0.2 and 0.02 per cent losses of uranium and thorium, respectively.[21] With 5*M* nitric acid–2*M* hydrochloric acid, uranium losses were 0.3 to 0.4 per cent. Losses were not increased by exposure of the core oxide to depleted Darex solution (1.3*M* nitric acid–1.5*M* hydrochloric acid–50 g of stainless steel per liter) for times up to 3 hr at boiling.

In scouting tests[21] Consolidated Edison fuel dissolved completely in dilute aqua regia containing fluoride catalyst, producing a solution from which uranium and thorium may be recovered by solvent extraction.

In a bench-scale test with unirradiated Yankee fuel samples (stainless-steel-clad uranium dioxide), the complete Darex standard flow sheet was successfully demonstrated; chloride was

removed to 440 ppm before dilution to flow sheet conditions.[12,20] With a fuel pin irradiated to 1000 Mwd/ton and decayed four months, the waste and recycle-acid streams contained approximately 0.01 per cent of the activity in the dissolver solution. A small quantity of solid residue from the dissolution and feed-adjustment steps, principally iron and silica as shown by analysis, contained no uranium. Over-all heat-transfer coefficients were 200 to 300 Btu/(hr)(sq ft)(°F) in a prototype steam-heated titanium feed-adjustment tank during the mixed-acid-removal and recycle-acid-recovery steps.

In Darex studies at HAPO[1-4] a number of trends have been observed during chloride removal from dissolver effluents:

1. The concentration of total chloride in the vapor phase exceeds that in the liquid if the acid concentration in the liquid is greater than the chloride concentration in the liquid.
2. The ratio of the vapor to liquid chloride concentrations is apparently inversely proportional to the chloride concentration in the liquid.
3. The presence of stainless steel hinders chloride removal.
4. Under "total" reflux conditions, the chloride removal rate varied markedly with boil-up rate, suggesting the possibility of a rate-limiting reaction in the vapor phase.

In another chloride removal study,[3] a solution of 2.2*M* uranium, 4.0*M* H^+, and 2.8*M* Cl^- was concentrated by a factor of 3, diluted to the original volume with 60 per cent nitric acid, and boiled under reflux for 2.5 hr. Excess nitric acid was removed by concentration. A chloride decontamination factor of 10^4 was obtained.

Studies on the effect of dissolver solution composition on chloride removal showed that the terminal chloride concentration after prolonged boiling with concentrated nitric acid increases with stainless-steel concentration. High concentrations of stainless steel (>1.25*M*) must be present to prevent attaining terminal chloride concentrations of 0.1 g/liter or less.[9] The presence or absence of uranium had little effect on the terminal chloride concentration attainable.

Chloride was removed from a 0.85*M* stainless steel and 0.8*M* uranium solution by sparging with nitrogen dioxide and air.[4] Chloride volatilized at the rate of 0.1 mole chloride per mole nitrogen dioxide added. Acid was produced at the rate of 0.7 mole H^+ per mole nitrogen dioxide added until the solution reached 6.1*M* H^+, after which no additional increase was obtained. Terminal chloride concentration was 1*M* compared with 0.2*M* for solutions containing uranium but no stainless steel.

3. *Aluminum Fuel Elements.* Studies have continued to determine dissolution rates of uranium-aluminum alloys in mercuric nitric acid mixtures.[7]

Six tons of NRX-irradiated uranium, five NRX plutonium-aluminum-alloy fuel assemblies containing 1.2 kg of plutonium, and 8.5 metric tons of BNL-irradiated uranium containing 4.9 kg of plutonium were processed at ORNL.[10] Feed for solvent extraction was prepared by continuous dissolution of metal in the metal recovery plant dissolver. To dissolve 0.5 ton of uranium per day, it was necessary to maintain a 200 per cent metal heel in the dissolver; 4.2 moles of nitric acid was consumed per mole of uranium, with 7.5*M* nitric acid as the dissolvent.

The average dissolution rate of the NRX alloy was in excess of 10 mg/(min)(sq cm) in 6*M* nitric acid catalyzed with mercuric nitrate; the final dissolver solution was 0.5*M* aluminum nitrate and 4.0*M* nitric acid.

General relations for performance of the tank-flow case for a flooded column dissolver have been developed[22] as an extension of work reported in an earlier Review[23] for the nonmixing or tube-flow case. The relations are applied to available pilot-plant data on the mercury-catalyzed dissolution of four shapes of 2S aluminum elements. The data cover a range of catalyst concentrations from 1.5×10^{-6} to 3.75×10^{-4}*M* Hg^+ and metal bed heights from 1 to 10 ft in a 2-in. pyrex column. The average initial dissolvent concentration was 5.6*M* nitric acid. Round rods, flat plates, tubes, and flattened tubes are compared. The data for the round rods are utilized to determine the effective reaction velocity constants at the various catalyst concentrations. The general dissolver equation is used to predict the effect on dissolution rate of the shape of metal elements, liquid phase flow rate, and height of the bed of elements. Calculated rates follow the trends in the data but not quite so well as calculated rates for the nonmixing or tube-flow case. The mathematical representation of the model is generally consistent with the pilot-plant data.

Dissolution of Dejacketed Material

If fuel jackets can be removed mechanically or the fuel sheared into pieces, dissolution of the irradiated core becomes a separate and possibly simpler feed preparation approach.

It was observed[2] that the presence of ferric nitrate increases the dissolution rate of uranium-molybdenum alloys, uranium metal, and uranium dioxide by nitric acid. The most pronounced increase in dissolution rate occurs at low acid where the dissolution in nitric acid alone becomes very slow. This property may be useful to shorten time cycles in batch dissolution to no heel.

Further studies on the preparation of Redox type feed solutions from uranium-molybdenum alloys by dissolution in nitric acid–ferric nitrate solutions may be summarized as follows:[3]

1. Off-gases from the dissolution of uranium–3 wt.% molybdenum alloy in ferric nitrate–nitric acid solution are primarily oxides of nitrogen. Only traces (less than 0.2 vol.%) of hydrogen were found.

2. Sulfate ion at concentrations which might be present during core dissolution due to incomplete washing following Sulfex decladding had no significant effect on uranium-molybdenum alloy dissolution in ferric nitrate–nitric acid solutions.

3. A laboratory-scale recirculating dissolver has been used for dissolution of uranium-molybdenum alloys. This equipment was operated with storage-vessel–to–dissolver-volume ratios from 10 to 20. Solution was maintained at 85°C in the storage vessel and preheated before it entered the dissolver. Normal dissolution rates and solution stabilities (as compared to runs in pot type dissolvers) were observed. Extensive (*ca.* 10 hr) recirculation of dissolver solution following dissolution to less than 0.2*M* free acid caused precipitation of a brown solid, presumably ferric hydroxide.

4. Stability (toward precipitation) of the dissolver solutions, during long term storage at 25 and 50°C, as a function of acidity, ferric nitrate, and uranyl nitrate concentration is under study. The minimum acidity for stable solutions is governed by the ferric nitrate concentration. Lower temperature favors stability of the solutions.

5. Aqueous ferric nitrate for use in this process can be prepared readily by dissolving mild steel in nitric acid. In dissolution rate studies covering ferric nitrate concentrations from 0*M* to 1*M* and nitric acid concentrations from 2*M* to 10*M*, dissolution rates for 1020 carbon steel ranged from 2 to 12 g/(hr)(sq cm). Ferric nitrate prepared in this manner has been used to dissolve uranium-molybdenum alloys, and the dissolver solutions have been used for plutonium oxidation and batch contact solvent-extraction studies.

6. Exploratory studies attempting to define the mechanism by which ferric salts prevent precipitation of uranyl molybdate are in progress. Preliminary evidence points toward formation of a soluble iron-molybdenum heteropoly acid.

Further studies on the dissolution of uranium–9 per cent molybdenum alloy in nitric acid–$Fe(NO_3)_3$ solutions were made.[4] The maximum uranium concentration which can be achieved during dissolution without solids formation is dependent on the terminal nitric acid concentration and increases from about 0.5*M* at 0.5*M* free acid to about 0.7*M* at 2.0*M* free acid. The acidity of the solutions at room temperature can be reduced to about −0.4*M* free acid with Diban without solids formation.

Ferric nitrate, at concentrations up to 1.0*M*, had no deleterious effect on the dissolution of Consolidated Edison 96 per cent thorium dioxide–4 per cent uranium dioxide sintered pellets in boiling 13*M* nitric acid–0.04*M* sodium fluoride–0.04*M* aluminum nitrate.[15]

Complete dissolution of 96 per cent thorium dioxide–4 per cent uranium dioxide core pellets in boiling 13*M* nitric acid–0.04*M* sodium fluoride–0.04*M* aluminum nitrate is achieved in 4 hr at a volume-of-dissolvent to weight-of-pellet ratio of 10. When this ratio is 3.5, complete dissolution is obtained in 15 hr.

Studies of the effect of radiolysis on the rate of attack of fuel core materials by the Sulfex medium (dilute sulfuric acid) were extended to more highly irradiated uranium dioxide.[4] It was found that uranium dioxide irradiated to a (calculated) exposure of 3000 Mwd/ton and cooled five months was attacked by boiling 4*M* sulfuric acid at a rate of only 0.02 per cent per hour. This corrosion rate is essentially identical to that found in earlier work with 500 Mwd/ton uranium dioxide cooled nine months, despite the fact that the measured radiation dose rate with the present material is greater by a factor of 7.5.

Dissolution of Zircaloy-uranium fuel in fused lead chloride continued to show promise.[19] Losses of uranium to the lead phase have been materially reduced by suspension of the fuel charge in the molten lead chloride. In comparable experiments metallic uranium was dissolved both by suspension and by permitting the uranium to float freely. Suspension of the charge reduced the uranium content of the lead product from 0.68 to 0.006 wt.% uranium.

The optimum dissolvent for the high-silicon aluminum-uranium dioxide Foreign Research Reactor fuel is 7.5*M* nitric acid–0.005*M* mercuric nitrate.[7] Use of this dissolvent results in a dissolver product 1.5*M* in aluminum nitrate and 1.3*M* in nitric acid, the correct composition for the subsequent gelatin treatment that will be used to remove silica from the feed solution.

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An annotated bibliography of reports on reprocessing of irradiated reactor fuels has been compiled by Jacobs,[1] and an addendum[2] brings the compilation up to May 1959.

Solvent Extraction

Modifications of Redox and Purex Processes

The Redox and Purex processes use methyl isobutyl ketone and tributyl phosphate, respectively, as extractants. These processes are currently employed in the recovery of uranium and plutonium from production reactor fuels. Work continues in an effort to improve these processes and to adapt them to the processing of nonproduction reactor fuels.

In the previous Review[3] it was noted that the capacity of the Hanford Purex uranium stripping column could be increased by operation with the organic phase continuous. However, the effect of these conditions on extraction efficiency was not reported. Pilot-plant data now available from ORNL suggest that other benefits may accrue from bottom interface operation. In processing of BNL-irradiated fuel, organic-continuous operation resulted in a tenfold improvement in decontamination of the plutonium product and a threefold improvement in decontamination of the uranium product. No mention was made of any adverse effect on product recoveries.[4]

Currently the principal development effort in Redox and Purex processing is in their adaptation to the recovery of fissile and fertile elements from spent nonproduction reactor fuels. The two major problems introduced by these fuels stem from the composition of the feed solutions and from the much higher radiation levels anticipated. In some cases the feed solutions contain significant quantities of inert diluent elements heretofore not encountered in processing production reactor fuels. In addition, radiation levels increased by more than two orders of magnitude will be encountered.

Development of a flow sheet for the recovery of uranium from Consolidated Edison type fuel is in progress.* The principal components of this fuel are urania and zirconium. Results of preliminary tests are available for a flow sheet based on extraction with 2.5 per cent TBP in kerosene (Amsco) and scrubbing with 1.0*M* aluminum nitrate. Synthetic active feeds were prepared by spiking with Purex aqueous waste. The decontamination factors observed in a small-scale batch experiment are presented in Table III-1. Separate first- and second-cycle feeds were prepared; therefore the decontamination factors are not additive. The process goal is a two-cycle over-all decontamination factor in the order of 10^8. Recycle of second-cycle aqueous waste to the first cycle is planned.[5–7]

Table III-1 DECONTAMINATION FACTORS FOR PUREX PROCESSING OF CONSOLIDATED EDISON FUEL[5–7]

Activity	First cycle	Second cycle*
Gross γ	3.5×10^5	7.6×10^4
Ru γ	2.9×10^4	3.0×10^4
Zr-Nb γ	1.8×10^5	6.3×10^4
TRE β	1.2×10^6	1.4×10^5

*Since separate feeds were prepared, the first- and second-cycle decontamination factors are not additive.

Redox processing is being considered for Darex feeds (stainless-steel fuels dissolved in 5*M* nitric acid–2*M* hydrochloric acid). Results have not been entirely satisfactory. The best decontamination factors realized thus far have been a factor of 4 lower than those obtained in Redox processing of production reactor fuels. The relatively high acid conditions required to prevent precipitation of stainless steel was the basic reason for the poor performance. Niflex feeds (prepared by dissolution in nitric acid–hydrofluoric acid mixture) subjected to Redox

*Under development at Oak Ridge National Laboratory.

processing were also poorly decontaminated. Decontamination factors were ½ of those noted for Darex feeds.[6,8]

Development work on Redox processing of uranium–3 per cent molybdenum alloy has progressed to the stage of tests with active feeds. Feeds were prepared by dissolution in a mixture of nitric acid, ammonium fluoride, and ammonium nitrate solution. Solution stability tests, batch contacting studies, and mixer-settler runs were made to investigate conditions for Redox processing. Using a feed containing aluminum nitrate to complex fluoride with an aluminum-to-fluoride mole ratio of at least 1.5, low product losses were realized. Uranium and plutonium losses in waste streams ranged from 0.05 to 0.2 per cent. The molybdenum concentration in the uranium product was less than 5 ppm of uranium. In studies of the effect of feed acidity on fission-product decontamination, it was noted that increased acidity resulted in poorer beta and gamma decontamination. As is characteristic of Redox processing, ruthenium comprised the major activity in the product streams.[9]

Data are available for Purex processing of a 9 per cent uranium-aluminum alloy in mixer-settlers. The goal, a fission-product decontamination factor of 4×10^8, was met in a two-cycle process. The first-cycle extractant was 6 per cent TBP, whereas that for the second cycle was 18 per cent TBP. Decontamination factors were 2×10^5 in the first cycle and 2×10^3 in the second cycle. The factor limiting decontamination was stated to be irradiation damage to the extractant.[10]

Studies of Alternate Extractants

A number of separations problems created by the power reactor fuels are not met adequately by the traditional Redox and Purex extractants. Methyl isobutyl ketone (Redox) suffers chemical damage at relatively low acid conditions. Tributyl phosphate (Purex), for all practical purposes, is suitable only for nitric acid systems. Therefore processes based on alternate extractants are being developed to increase capacity, to improve separation, to improve radiation and chemical stability, and to permit the recovery of by-products from the waste streams.

Work applicable to alternate Redox solvents is reported on the diethers in which the two ether oxygens are separated by 4 to 6 CH_2 groups. These extractants provide higher flash points and better resistance to nitric acid than hexone. Batch tests indicated some advantages of the diether over hexone with respect to fission-product decontamination.[11] Relative to hexone, dimethoxypentane provides better uranium extraction but poorer fission-product decontamination. With methoxybutoxypentane the uranium distribution ratios were somewhat less favorable but fission-product decontamination was improved.

The extraction of uranium from acidic sulfate solutions with tri-*n*-octylamine in benzene was studied. At low uranium concentrations a monomeric organic complex was formed. Between 0.0257*M* and 0.762*M* sulfuric acid the equilibrium variation in equivalents of amine per mole of uranium (loading) was not significant being between 4.1 and 5.2. The data further indicated that over a wide range the organic loading was a function of the aqueous phase uranium activity and relatively independent of the amount of benzene diluent present.[12]

Mono-2-ethylhexyl phosphoric acid in xylene diluent is being considered for the separation of americium and cerium from rare-earth activities. In a chloride system with an aqueous phase of 12*M* hydrochloric acid contacted with 0.5*M* 2-ethylhexyl phosphoric acid, distribution coefficients, E_a^o, were 0.12 for cerium and 0.025 for americium or a separation factor of 5. Separation factors increased with increasing atomic weights being 7 for neodymium, 8.5 for promethium, and 10 for europium. The results presented are for tracer quantities of americium and rare earths. For macro amounts, the distribution coefficients varied with the inverse cube root of the rare-earth concentration.[4]

The recovery of neptunium in the Purex system with dibutylbutyl phosphonate (DBBP) has been studied in batch tests. In equilibration of 30 per cent DBBP with synthetic aqueous waste, neptunium distribution ratios of 9.9, 1.8, and 3.3 were obtained at nitric acid concentrations of 4*M*, 7*M*, and 2*M*, respectively. With 30 per cent TBP the distribution ratios were considerably less favorable being 0.2 and 1.0 in 4*M* and 7*M* nitric acid.[11]

In studies of the extraction of fission products strontium, cerium, and cesium from neutralized synthetic aqueous waste, data are available comparing 4 per cent tall oil in chloroform and 3 per cent di-2-ethylhexyl phosphoric acid (D2EHPA). Cerium extraction was about 50 per cent by

D2EHPA at pH 8 and by tall oil at pH 9. An unfortunate side effect was the apparent organic phase solubilization followed by aqueous phase precipitation of the remaining activity. The maximum cerium distribution coefficients, E_a^o, were about 10^3 for both extractants. The maximum strontium E_a^o was 97 for tall oil and 11 for D2EHPA.[11]

The removal of aluminum from aqueous solution is of interest in the processing of aluminum alloy fuels. Some preliminary data indicate that aluminum can be extracted from nitrate solution with acetyl acetone in carbon tetrachloride diluent. Aluminum was stripped from the organic phase with 2*M* nitric acid. Nickel and chromium were not extractable from nitrate solution by acetyl acetone.[13]

or their tendency to form emulsions which limit column capacity. Considerable effort is being devoted to the study of solvent degradation.

The most commonly used TBP diluent, kerosene, is subject to chemical degradation. The results of an extensive study of chemical degradation of kerosene diluent are available.[14] In general, previous findings were confirmed. Wide variations in the degree of resistance to chemical attack were noted as a function of paraffinic, isoparaffinic, aromatic, and olefinic hydrocarbon content. Adverse effects were noted in the presence of strong nitric acid and in the presence of small amounts of nitrous acid. The nonparaffinic hydrocarbon content and the nitrous acid content of the aqueous phase were found to be the most significant variables.

Table III-2(a) SUMMARY OF IRRADIATION STUDIES OF VARIOUS EXTRACTANTS[7,11,15]

Extractant*	Radiation dose, watt-hr/liter	Yield of decomposition products, G†			
		Decomposed	Polymerized	Total gas	Hydrogen
NBHDA	200	2.14	1.81	1.85	1.79
Alamine	400	3.49	2.20	3.10	2.98
TLA	400			2.98	2.92
TIOA	400			2.94	2.68
Primene JM-T	400	2.25	1.50	2.94	2.30
TOPO	400	4.10	2.78	1.82	1.77
TBP	300			1.87	
TBP saturated with 12*M* HNO_3	100			1.45	
TBP saturated with 12*M* HNO_3	400			2.76	

*NBHDA = n-benzylheptadecyl amine; alamine = trioctyldecyl amine; TLA = trilauryl amine; TIOA = triisooctyl amine; TOPO = tri-n-octylphosphine oxide.

†G = molecules formed per 100 ev of radiation absorbed.

Table III-2(b) COMPARISON OF DBPP* AND TBP

Extractant	Radiation dose, watt-hr/liter	Double bond yield, G†
4.5% TBP in Amsco	400	3.37
100% TBP	400	1.00
15% TBP in Amsco	200	4.08
15% DBPP in Amsco	200	3.51
100% DBPP	200	0.36

*DBPP = dibutylphenyl phosphonate.

†G = molecules formed per 100 ev of radiation absorbed.

Solvent Degradation

Process extractants and diluents are degraded by chemical and radiation damage. Many of the degradation products are objectionable because of their undesirable extraction characteristics

Paraffinic hydrocarbons were the most stable diluents. The diluent degradation products were mainly carboxylic acids, organic nitrates, and nitro and nitroso compounds. The conventional solvent recovery treatments, sodium carbonate and nitric acid washing, were found to be only partially effective in removing the degradation products.

Studies of radiation damage to process solvents emphasize irradiation levels in excess of 200 watt-hr/liter to provide information applicable to processing of high burn-up nonproduction reactor fuels. In many cases the newly developed organonitrogen and organophosphorus extractants have proved to be equally or more resistant to radiation than the traditional Redox and Purex extractants. Recent data appear in Tables III-2(a) and III-2(b).

Some data are presented for environments closely approximating anticipated process conditions. TBP saturated with nitric acid forms an equimolar complex $TBP \cdot HNO_3$. Tests showed that the rate of gas formation under irradiation was not significantly higher for the complex than for pure TBP. However, the acidic products from the radiolysis of the $TBP \cdot HNO_3$ complex were found to complex from 20 to 100 per cent more rare-earth activity than the radiolysis products of pure TBP. Other tests emphasized the need for a careful appraisal of diluent stability. For example, the rate of double bond formation on irradiation was more than a factor of 3 higher for TBP diluted with Amsco (kerosene) than for pure TBP. The adverse effect of the diluent was even greater for dibutylphenyl phosphonate. Most proposed flow sheets specify diluted extractants. Based on demonstrated technology, cost, and availability, the choice has largely been restricted to various kerosene fractions.[7,15,16]

In other tests the effect of aromatic compounds in solutions of 30 per cent TBP in Amsco was studied. The aromatic additives were 5 or 10 per cent isopropyl biphenyl or naphthalene. The solutions were saturated with 2*M* nitric acid and irradiated to 200 or 400 watt-hr/liter. The aromatic compounds did not affect appreciably the amount of total gas or monobutyl phosphoric acid produced.

Fundamental Solvent-extraction Studies

Work on the identification of solute species, the estimation of activity coefficients, solvent-diluent-aqueous phase interactions, transfer mechanisms, and studies of fission-product behavior have been reported.

Solutions of di-2-ethylhexyl phosphoric acid (D2EHPA) and trioctyl phosphine oxide (TOPO) in *n*-octane were studied to determine the solvent-extraction behavior, to determine the solute species present, and to estimate activity coefficients. The results indicated that D2EHPA exists primarily as a stable dimer with the possibility of some trimerization at low concentrations.[17]

Isotopic exchange rate measurements are in progress to investigate the mechanism of uranium transfer. The equipment features an hourglass-shaped two compartment vessel. A relatively stable fixed-area interface can be maintained at the juncture during stirring of the individual bulk phases. Measurements were made of the rate of exchange of U^{233} between phases of TBP in dodecane and uranyl nitrate in water.[13]

A principal limitation to Purex decontamination is ruthenium activity retained in product streams. The results of a thorough investigation of the behavior of retained ruthenium are available. The anomalous behavior of ruthenium was explained on the basis of the existence of several species in Purex feed. The more extractable species limit the separation of ruthenium from uranium and plutonium.

Small fractions of ruthenium and zirconium-niobium show anomalous extraction behavior in the Purex process. Most of the ruthenium exhibits normal behavior for which the distribution coefficient, E_a^o, between 30*M* per cent TBP and 3*M* nitric acid is about 0.001. A small fraction representing two species has E_a^o values of about 2.0 and 0.2 and is extracted in appreciable quantities at low organic phase uranium concentrations. The distribution coefficient for extractable ruthenium increased with decreasing temperature, and its relative abundance increased with increasing feed nitric acid concentration. Attempts to precipitate the extractable ruthenium as the dioxide or to carry it on ruthenium dioxide were unsuccessful.[18]

Precipitation Processing

Before separating uranium and plutonium from fission products by solvent extraction, it is sometimes desirable to treat the solution of irradiated uranium by some simple process to remove materials that cause emulsification in the extractors and to reduce substantially the amount of certain fission products, particularly zirconium and niobium. In the Purex process these objectives can be achieved by precipitating manganese dioxide which scavenges considerable portions of the insoluble impurities and fission products. The precipitation is accomplished by the addition of a solution of potassium permanganate to the feed solution which contains a slight excess of manganese nitrate.

The usefulness of this process requires that the precipitate be easily separated from the supernatant. Manganese dioxide precipitates are frequently bulky and settle slowly; they can be centrifuged but with some difficulty. Laboratory studies concerned with decreasing the bulk

and increasing the settling rate have been carried out.[19,20]

In nitric acid solutions of uranium or uranium-aluminum alloy, precipitation with vigorous mixing (25 hp/1000 gal) produced a precipitate with a smaller bulk volume and larger particle size than precipitates formed under normal mixing (0.05 hp/1000 gal). Semiworks tests showed that the improved precipitate can be processed through a large centrifuge about twice as fast as a precipitate formed at lower power. No change was detected in the ability of the precipitate to scavenge fission products.

In acidic solution the bulk volume of the precipitate was only slightly affected by variations in temperature and acidity. In solutions of uranium-aluminum alloy, however, the volume of the precipitate was increased sixfold when the manganese dioxide was preciptated in solutions that were 0.8*M* acid deficient. Decontamination factors for gamma activity in tracer-level experiments increased from 3.5 to 8.0 as the acidity was decreased from 1.0*M* free acid to 1.3*M* acid deficient.

Ion–exchange Processes

Ion-exchange processes have been applied to recovery of plutonium and neptunium, uranium, americium, and actinide elements and to the removal of radioactive zirconium and ruthenium from process solutions.

Ion-exchange Processes for Purification of Plutonium and Uranium

Previous Reviews[3,21–24] have discussed purification of plutonium by ion exchange. Hart et al.[25] have made a semitheoretical study of the chemistry of anion-exchange processes. Pseudo equilibrium constants were obtained for the systems Pu(III)-Dowex 50, Pu(III)-Dowex 50-W, and Pu(IV)-Dowex 1, in nitric acid solution. Exchange height equations have been obtained for the Pu(III)-Dowex 50 and the Pu(IV)-Dowex 1 systems. Elution equations are given for the systems Pu(III)-Dowex 50 and Pu(III)-Dowex 50-W. The elution of plutonium from anion-exchange resins is fairly rapid with a reducing agent but slow without one. A fairly complete study of elution with dilute acid is given by Ryan and Wheelwright[26] in an expanded version of their Geneva paper which was reported in a previous Review.[24] They report that sufficiently rapid rates of elution can be obtained at elevated temperatures without the use of reducing agents.

Cation exchange may be used to concentrate the dilute (<10 g/liter) U^{233} or plutonium products which are obtained from solvent-extraction processes.[28] Losses of fissionable material are less than 0.01 per cent, and some separation of the products from fission and corrosion products is achieved. Two ion-exchange processes are considered:

1. Plutonium concentration and purification from low levels of fission products by adsorption of Pu(III) on a cation-exchange resin. This process is applicable to the plutonium nitrate recovered by solvent extraction from irradiated fuels.
2. The final concentration and purification of U^{233} as uranyl nitrate from a solvent-extraction process. Plutonium and uranium concentration factors of about 250 are obtained.

Laboratory investigations with cation- and anion-exchange resins for the final purification of plutonium from traces of uranium, iron, and fission-product zirconium are described.[29] On the basis of these results the nitric acid–plutonium stream from a solvent-extraction cycle may be adsorbed on a cation resin as Pu(III) and eluted with hydrochloric acid; iron and uranium are removed by passage of this solution through an anion column, and further purification of plutonium is achieved by its adsorption as Pu(IV) on a second anion column.

Purification and Recovery of Neptunium

Papers by Nairn and Collins[29] and by Flanary and Parker[30] report on processes for purification of neptunium by ion exchange. The process outlined by Nairn and Collins consists of conditioning of solvent-extraction stock solution with nitric acid, concentration by anion exchange, adjustment to Np(IV), and purification by TTA extraction and anion exchange.

The plant design flow sheet for a two-stage ion-exchange plant for concentration of neptunium from stock solution is shown in Fig. 2.

Flanary and Parker[30] describe a process whereby gram quantities of Np^{237} were recovered from irradiated natural uranium, irradiated enriched uranium, and fluorination ash from depleted uranium by extraction with tributyl phosphate. For natural uranium a modified Purex

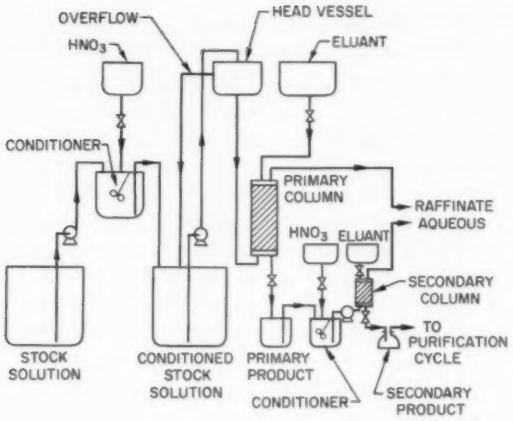

Figure 2—Diagrammatic flow sheet for concentration of neptunium by a two-stage anion-exchange process.[29]

flow sheet with simultaneous extraction of plutonium, uranium, and Np(VI) and partitioning by acidity adjustment is used. Final concentration and purification are done by ion exchange. For enriched uranium the Neptex process, which is similar to the 25-TBP process, is used. There is no plutonium present and neptunium is extracted in the tetravalent state. The process used with fluorination ash is similar to the Neptex second cycle.

The Np(IV) in the Pu(III) product stream from the second cycle along with the plutonium and residual uranium are sorbed on a Dowex-50 column as nitrates. The loaded column is treated with a small amount of 0.25*M* sulfuric acid containing 0.05*M* hydroxylamine sulfate to remove the uranium. Some neptunium will be eluted with the uranium. Increasing the eluant sulfate concentration to 0.5*M* results in rapid and complete elution of the remaining neptunium, just ahead of the plutonium, although some of the neptunium may go into the plutonium product. The sorption may be repeated and the neptunium eluted with nitric acid solution to give a relatively pure (99.9 per cent) neptunium solution.

Further purification from plutonium can be effected by an ion-exchange procedure based on uncomplexed Pu(III) chloride and complexed Pu(IV) nitrate.[30] In a single anion-exchange adsorption of the Np(IV) chloride complex, Pu^{239} was removed as trivalent plutonium by reduction with sulfur dioxide and elution with 12*M* hydrochloric acid saturated with sulfur dioxide.* This step also successfully removed calcium, rare earths, americium, and curium. The neptunium was eluted with 1*M* to 3*M* hydrochloric acid.

Miscellaneous Ion-exchange Studies

Distribution coefficients of americium onto Dowex-1, X-4 (50 to 100 mesh) were measured from several aluminum and calcium nitrate solutions and from simulated Redox wastes.[31] Log K_D was found to increase linearly with nitrate concentration from 4.0*M* to 8.0*M* nitrate in aluminum nitrate (ANN) and in ANN made acid deficient with calcium carbonate or ammonium hydroxide. Distribution coefficients were lower in acid deficient solutions and were higher at 25°C than at 70°C. K_D reaches 200 at 25°C and 70 at 70°C in 7.9*M* nitrate in neutral ANN. Simulated Redox first-cycle aqueous waste in which the dichromate was destroyed by hydrazine nitrate gave a K_D of 160 at 25°C and 70 at 70°C. Equilibrium appeared to be reached reasonably rapidly. These values of the K_D indicate that americium could be recovered from Redox waste by anion exchange. It can be expected that total rare earths would load to about the same degree as americium and a rare earth–americium concentrate would be obtained. The practicality of such a process depends on several incompletely explored factors such as radiation stability of the resin and removal of solids from the feed.

Equilibrium uranium loadings have been determined[32] for Dowex 21K anion-exchange loadings using from 0.3*M* to 0.5*M* sulfate solutions at pH 2. The results at a given sulfate concentration could be fitted by a Langmuir sorption isotherm. For 0.3*M* sulfate the Langmuir constants were $A = 1.33$ liters per gram of dry chloride-form resin and $B = 1410$ liters per mole of uranium. For 0.5*M* sulfate the A and B values were 0.86 and 920, respectively. The rates of uranium loading from 0.025*M* to 0.20*M* sulfate were measured, and apparent uranium

*The reduction of plutonium by sulfur dioxide may be incomplete; however, the addition of a small amount of ferrous chloride to the hydrochloric acid wash will test for incomplete reduction and will remove residual plutonium.

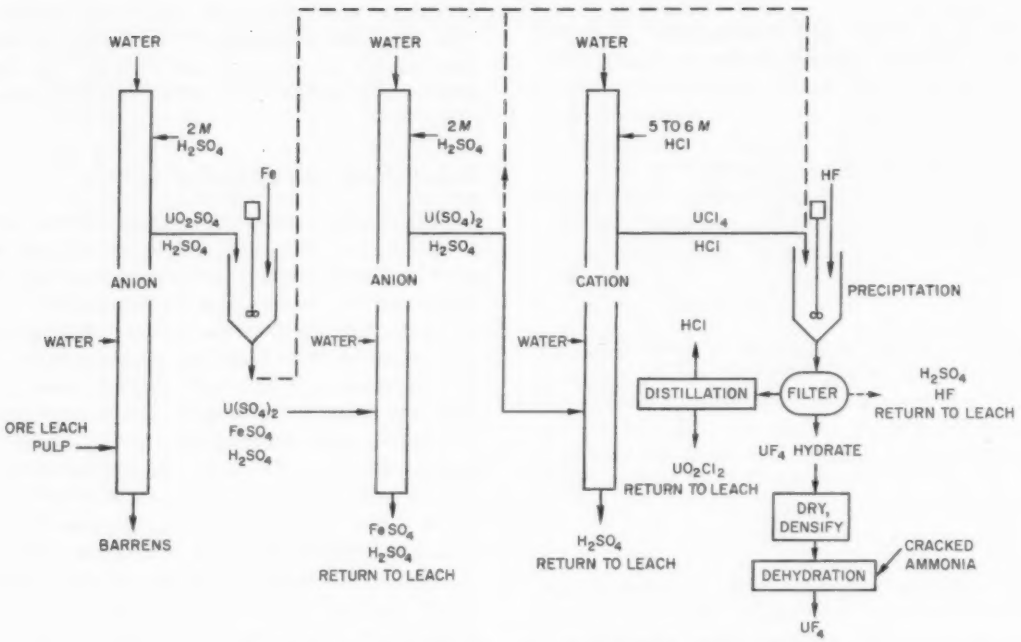

Figure 3—Proposed ore-leach-sulfate-iron flow sheet.[35]

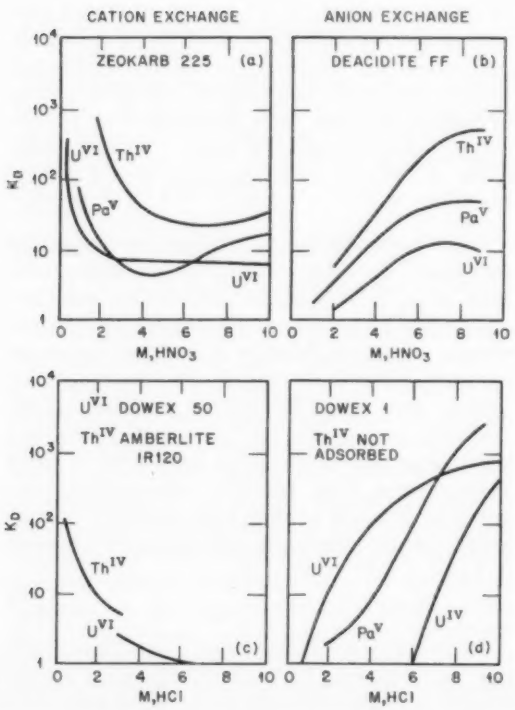

Figure 4—Ion-exchange data for Th(IV), Pa(V), and U(IV and VI).[36]

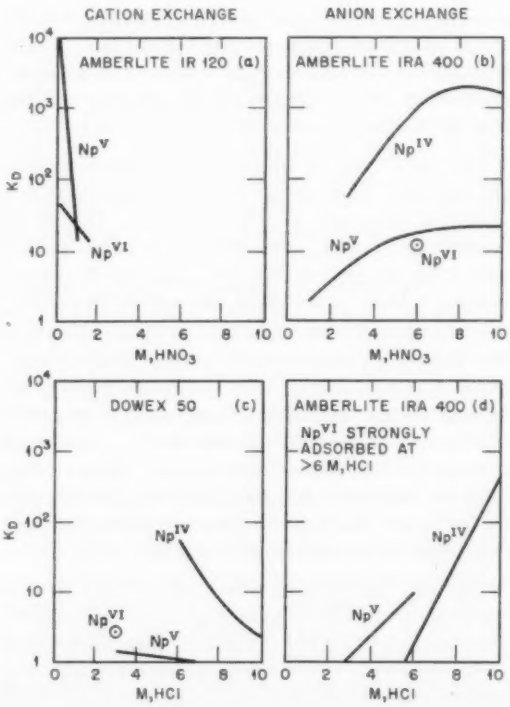

Figure 5—Ion-exchange data for Np(IV, V, and VI).[36]

diffusion coefficients in the range 1.2×10^{-7} to 1.6×10^{-7} cm^2/sec were calculated.

The rate of sorption of uranium into 40-μ Dowex 21K resin particles from a 0.0042*M* uranyl sulfate solution was studied by measuring the uranium loading on individual beads as a function of time.[33] The beads became loaded to one-half their equilibrium value in 24 min, and the "apparent" over-all diffusion coefficient was 9×10^{-8} cm^2/sec. A half time of 30 min for uranium anion exchange was measured in differential bed studies of uranium sorption on Dowex 21K.[34]

A uranium sulfate process flow sheet for the production of uranium tetrafluoride from sulfate ore leach liquors is presented by Holcomb.[35] The uranium is sorbed on an anion-exchange resin from 0.2*M* sulfate ore leach and eluted with 2*M* sulfuric acid. Iron powder reduces UO_2SO_4 to $U(SO_4)_2$ which is then sorbed on anion-exchange resin to separate it from the iron and eluted from the anion exchange resin with 2*M* sulfuric acid. The resulting $U(SO_4)_2$ is sorbed on a cation-exchange resin from the sulfuric acid solution and eluted from the resin with 5*M* to 6*M* hydrochloric acid. The uranium tetrachloride thus produced may be treated with stoichiometric amounts of hydrofluoric acid to precipitate $UF_4 \cdot {}^3/_4\ H_2O$. This continuous ion-exchange flow sheet is presented in Fig. 3.

Ion-exchange data for the actinide elements in nitric and hydrochloric acid solutions are summarized by Hardy[36] (see Figs. 4 and 5). The data are of interest for the processing of solutions and also for the comparison of the ion-exchange behavior of these elements in their various valence states.

Recent publications in ion exchange were summarized by Kunin and Bodamar.[37] Important trends in the ion-exchange field for 1958 are essentially an outgrowth of developments initiated in recent years. Atomic energy is expanding ion-exchange utilization in all directions, including uranium recovery from low grade ores, water treatment in primary and secondary reactor loops, and waste treatment. "Liquid ion exchangers" for recovering uranium from leach liquors are now established. Multiple permselective membrane cells for treating brackish water supplies are of prime interest because of the need for potable and irrigation water in many areas of the world. Several large commercial units will begin operation in 1959.

Volatility Processes

Process Combining Fluidization and Fluorination Techniques

In a previous Review[23] ADF processes which involve *aqueous dissolution* of the fuel, *drying* of the solution to solids, and subsequent fluorination of the fissile elements were described. Development work is being carried out on an engineering scale to apply some of these process techniques to enriched uranium-zirconium alloys. Laboratory work is also being done on application of the process to uranium-plutonium fuels. For the zirconium alloys the process involves dissolution of the alloy in aqueous hydrofluoric acid, followed by conversion of the metal to dry granular material. The solids are then fluorinated in a fluid-bed reactor to remove the uranium as the volatile hexafluoride.

A 6-in.-diameter fluid-bed dryer has been used to prepare material for fluid-bed fluorination studies.[38,39] The feed solutions contained about 1.4*M* zirconium, 6.3*M* fluoride, and either 0.03*M* or 0.013*M* uranium as uranyl fluoride, equivalent to 5 and 2 wt.% uranium alloy, respectively. Bed temperatures of 300 and 450°C were used. Fluidizing gas velocity was maintained at 2 ft/sec. No operating difficulties were encountered but particle growth occurred in all runs. Feed rate unexpectedly had no effect on the particle growth rate. Two runs in which 25 per cent of the fluidizing air was introduced into the bed through a separate jet designed to produce particle attrition showed little or no particle growth.

Some difficulty is still being encountered in removing uranium from the dryer product by fluorination. A number of experiments investigating various operating variables have been made in a 2.5-in.-diameter Monel reactor. Recent data are shown in Table III-3.

The use of fluidized beds for carrying out highly exothermic gas-solid reactions is being considered at BNL.[40–42] Results on the reaction of anhydrous HCl with coupons cut from Zircaloy-clad, zirconium-uranium fuel-element plates consistently show reaction rates of 4000 to 6000 mg/(sq cm)(hr) with fluidized-bed temperatures ranging from 400 to 450°C. Under these conditions the temperature of the metal coupon did not exceed that of the bed by more than 60°C. Results on the reaction of fluorine (65 per cent F_2, 35 per cent He) with metallic

Table III-3 EFFECT OF OPERATING VARIABLES ON REMOVAL OF URANIUM FROM URANIUM-ZIRCONIUM POWDERS[38]

Equipment: 2½-in.-diameter Monel column
Fluidizing gas composition: 15% F_2, 85% N_2
Fluidizing gas velocity: ~1 ft/sec

Fluorination run No.	Effect studied	Fluid-bed dryer conditions: U conc. in feed (alloy equivalent, wt.%)	Fluid-bed dryer conditions: Temp., °C	Fluorination temp., °C	Original uranium removed, %: After 4 hr	Original uranium removed, %: After 8 hr
U-Zr-15*	Preheating in nitrogen at 600°C for 7 hr	5	240	500	88	89
U-Zr-11*	No preheating	5	240	500	88	98
U-Zr-13†	Fluorination temp.	3.5	300	500	50	61
U-Zr-16†	Fluorination temp.	3.5	300	600	92	97
U-Zr-18‡	Drying temp.	5	450	500	56	60
U-Zr-11*	Drying temp.	5	240	500	88	98

*Starting material expected to be ZrF_4 with ZrO_2 core.
†Starting material expected to be primarily ZrF_4 with about 1 per cent Sn.
‡Starting material expected to be ZrO_2 and $ZrOF_2$.

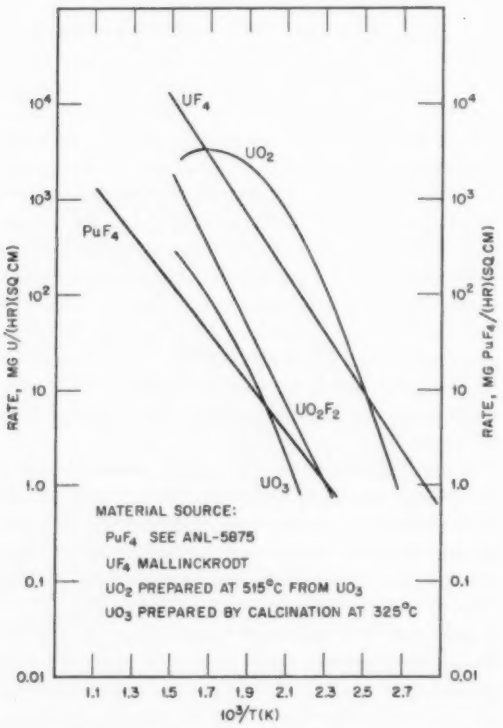

Figure 6—Rate of fluorination of uranium and plutonium compounds. (Prepared at Argonne National Laboratory.)

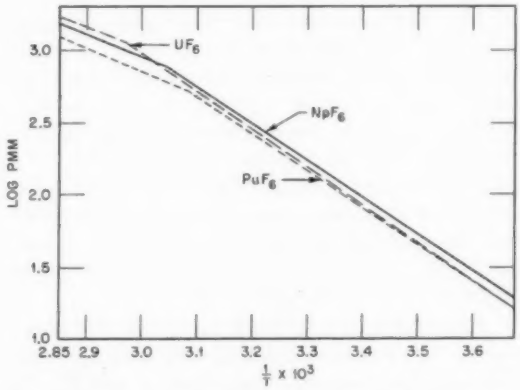

Figure 7—Vapor pressures of the hexafluorides of uranium, neptunium, and plutonium.[46]

Table III-4 THERMODYNAMIC PROPERTIES OF THE HEXAFLUORIDES OF THE ACTINIDE ELEMENTS[46]

	Boiling or subl. pt., °C	Triple point: °C	Triple point: mm Hg	Heat of fusion (cal/mole)	Entropy of fusion (cal/mole)(deg)
UF_6	56.54	64.05	1139.6	4588	13.61
NpF_6	55.18	55.10	758.0	4198	12.79
PuF_6	62.16	51.59	533.0	4456	13.72

uranium (1 × 2-in. coupons) show reaction rates in excess of 2700 mg/(sq cm)(hr) with bed temperatures of 450°C. In these experiments, involving some 15 g uranium, this otherwise violent reaction was clearly under control.

Process Chemistry of Fluoride Systems

The rates of fluorination of a number of compounds of uranium and plutonium have been de-

termined. The equipment, procedures, and results have been described in detail.[38,43–45] The results are summarized in Fig. 6.

The vapor pressures of neptunium hexafluoride and plutonium hexafluoride have been measured from 0 to about 77°C with a quartz sickle gauge.[46] The results are compared with those for uranium hexafluoride in Fig. 7. The triple points, boiling or sublimation points, heats of fusion, and entropies of fusion are compared in Table III-4.

Pyrometallurgical Processing

Several sites are working on pyrometallurgical processes in anticipation that such processes will provide reduction in fuel processing costs. This anticipation rises principally from the elimination of chemical conversions and the ability of such processes to handle short-cooled fuels.

Melt Refining

To provide information on the performance and economics of a pyrometallurgical process, ANL is building a pilot plant contiguous to the Second Experimental Breeder Reactor (EBR-II) now under construction at the National Reactor Testing Station in Idaho. The process to be used initially is melt refining* which has been intensively studied for several years at Argonne.

The contract for construction of the fuel cycle facility was awarded recently by the AEC to Diversified Builders, Inc., Paramount, California.[47] With 18 months allowed for construction and about a year for installation and testing of equipment, processing of irradiated fuel should begin in 1961. Construction of the laboratory and service building on the same site is about 80 per cent complete.

Meanwhile, procurement and testing of equipment components is continuing at Argonne. Molybdenum disulfide has not been a satisfactory dry lubricant for the prototype manipulator now under test at Argonne. All dry lubricated bearings have been repacked with Shell APL radiation-resistant grease. Bearings so lubricated have been irradiated to a total dose of 8×10^8 rad, with no appreciable change in consistency of the grease. Formal bids will be solicited soon for eight operating manipulators.

The initial fuel loading of the EBR-II reactor is now being prepared using prototype equipment for the fuel processing facility. Sixteen 10-kg ingots of enriched "fissium" alloy have been prepared in the melt-refining furnace. Analytical results indicate homogeneous ingots with compositions close to those calculated from material additions (see Table III-5). Isotopic analyses for the first 15 ingots averaged 48.3 and ranged from 48.2 to 48.5 ± 0.5 wt.% U^{235}. It is believed that this demonstrates the feasibility of fuel blending by this procedure in the prototype equipment. Yields for the ingots have ranged between 95 and 97 per cent and have averaged 96 per cent.

Table III-5 HOMOGENEITY OF EBR-II FUEL ALLOY PREPARATIONS[47]

Element	Nominal composition, wt.%	Ingot sample concentration, wt.%
Molybdenum	2.46	2.43 ± 0.11
Ruthenium	1.96	2.14 ± 0.12
Rhodium	0.28	0.27 ± 0.025
Palladium	0.19	0.19 ± 0.011
Zirconium	0.10	0.09 ± 0.018

Although the initial EBR-II fuel charge will be enriched uranium alloy, plutonium fuel alloys will be employed subsequently. The melt-refining behavior of such alloys is therefore of great importance. Five melt-refining experiments have been made with 20 per cent plutonium−10 per cent fissium-uranium alloys.[48] The metal was liquated 3 to 5 hr at 1300 to 1400°C, during which time the average plutonium concentration in the ingot decreased at a rate of about 0.1 per cent per hour (from 20.0 to 19.7 per cent in 3 hr). Thus the plutonium loss in a melt-refining step would be only about 10 per cent larger than the uranium loss. Two experiments in which cerium was added to the melt indicate that cerium removal during melt refining is not affected appreciably by the presence of plutonium. In two other experiments carbon was added to remove zirconium by carbide slagging. The carbon appeared to have no appreciable effect on the plutonium behavior.

*The term melt refining refers to melting of certain uranium and plutonium fuels in ceramic crucibles under conditions which provide for fission-product removal by volatilization and formation of stable drosses.

A number of reports have been issued which pertain to work on an engineering-scale demonstration of remote processing and refabrication — Pyrometallurgical Refabrication Experiment (PRE) — of irradiated uranium fuel from SRE type reactors. (As mentioned in the previous Review,[3] this work has been discontinued.) Design and operation of a remotely operable vacuum-casting furnace for production of fuel rods has been described.[49–51] The furnace was designed to remelt a decontaminated metal ingot, to permit re-enrichment, and to centrifugally cast the metal into fuel rods. Related problems of lighting, viewing, manipulator design, special handling devices and tools, and instrumentation were also discussed. The experience and information gained in mock-up operations were translated into a conceptual design for an in-cell furnace for use in future hot cell facilities.

A rod fabrication device was tested for fabrication of SRE fuel rods, entirely by remote control, using pyroprocessed metallic uranium fuel. By means of the device, six stainless-steel fuel cans could be loaded with fuel slags, outgassed, partially filled with NaK, and a stainless-steel cap welded on top of each can. Design also permitted remote maintenance and replacement, in-cell, of any mechanical component of the assembly. In the experimental program short dummy fuel rods were consistently made with leaktight and structurally sound welds. Conclusions resulting from these tests were that (1) the mechanisms should be remotely maintained by complete replacement of actuating assemblies rather than by attempting to replace small parts, (2) a simple means of remotely replacing dynamic shaft seals should be devised, and (3) it is important that good control of welding conditions be consistently maintained.

Liquid Metal Processes

Rather intensive effort is being devoted to processing of fuel material in liquid metal media, particularly at ANL, where, in connection with the EBR-II program, processes are being developed for recovery of fissionable materials and for isolation of plutonium from blanket materials. Solvent metals generally employed are aluminum, magnesium, mercury, zinc, and cadmium. The separations processes envisioned involve dissolution of the irradiated fuel in a liquid metal solvent followed by separation of fissile material from fission elements by combinations of crystallization and extraction with immiscible metals and molten salts. Recovery of the fissile metal will probably be accomplished by vaporization of the solvent metal.

Additional solubility data as a function of temperature and composition and various thermodynamic data have been reported by several sites for cadmium- and zinc-based systems (references 39, 47, and 52 to 54). The thermodynamic data include characterization of intermetallic phases, determination of the free energies of their formation, and measurement of the activity coefficients of solute elements in liquid metal media. Isothermal solubilities in liquid zinc and cadmium of the metallic elements of atomic

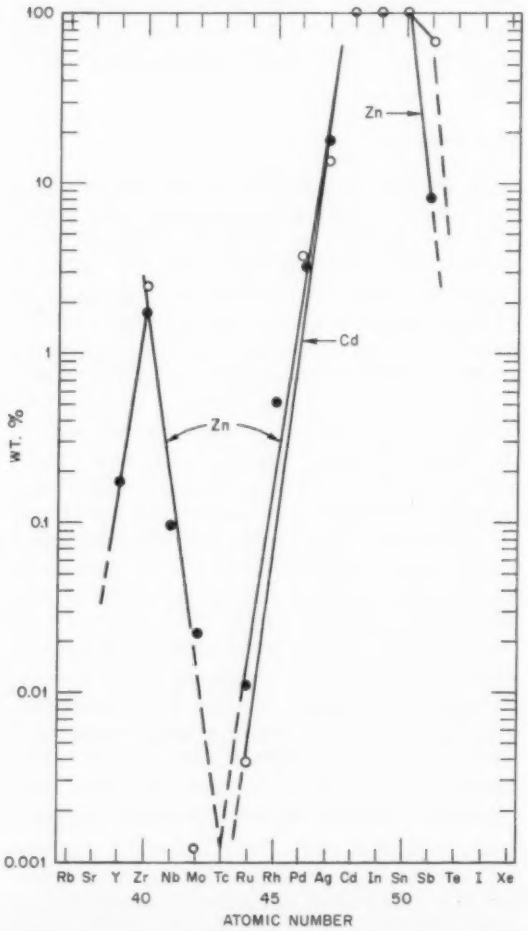

Figure 8 — Periodicity of solubility in liquid metals.[47] ○, 500°C; ●, 600°C.

numbers 37 to 58 have been found to be a rather striking function of atomic number (see Fig. 8). A maximum solubility was observed at zirconium and minimum solubility is predicted for technetium.

Measurement of solute element solubilities in mercury is in progress at Oak Ridge National Laboratory.[16,33] Recently, the solubility of plutonium in mercury over the temperature range 20 to 325°C was reported.[55] The plutonium solubility increased from 2.1 g/liter at 20°C to 85.7 g/liter at 325°C.

The cadmium systems are receiving principal attention at Argonne because of the favorable corrosion behavior in mild steel and 400-series stainless-steel equipment. Confirmation of the favorable corrosion with cadmium was provided by the virtual absence of corrosion in long-time (1000 hr) dynamic corrosion tests at 500°C of mild steel by cadmium, cadmium–2 per cent uranium, cadmium–5 per cent magnesium, and cadmium–8 per cent zinc–0.2 per cent magnesium alloys. The results are considered very encouraging. Trouble-free operation of a mild steel corrosion loop circulating a cadmium–2 per cent uranium–0.2 per cent magnesium solution at 550°C has been experienced in the first 200 hr of a 1000-hr test. Ability to use mild steel equipment has resulted in acceleration of engineering studies on dissolution, distillation, retorting, and separation of insoluble phases. Design is almost complete on a full-scale distillation unit capable of distilling up to 100 kg of cadmium per hour.[47]

The solubility of uranium in mixed solvents is now under study.[39,47] The striking effects of composition on uranium solubility are further evidence of the flexibility in process conditions available through use of liquid metal solvents. The low uranium solubility in metal solutions having relatively high magnesium concentrations has been mentioned in previous Reviews as being the basis for separation of uranium from plutonium, thorium, and rare-earth elements since the latter have relatively high solubilities in such solutions. The effect on uranium solubility of magnesium concentration in zinc is shown in Fig. 9. A similar, but less pronounced, effect is also observed in the magnesium-cadmium system (Fig. 10). The decreases in uranium solubility are associated with change in the crystallizing species from U_2Zn_{17} or UCd_{11} to uranium metal.

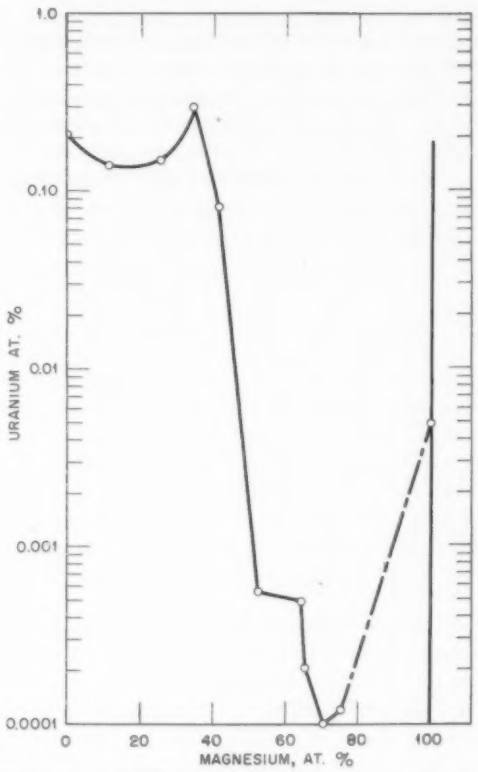

Figure 9—Solubility of uranium in zinc-magnesium alloys at 680°C.[39]

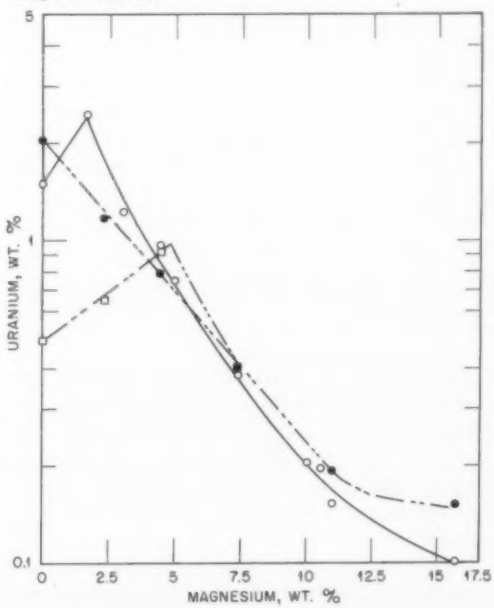

Figure 10—Effect of magnesium on the solubility of uranium in cadmium.[39] □, 400°C; ○, 450°C; ●, 550°C.

The isothermal addition of zinc to uranium-cadmium solutions at low temperatures (325 to ~475°C) causes uranium to precipitate as U_2Zn_{17}. The solubility of uranium drops sharply after the addition of as little as 1 per cent zinc, and precipitation of uranium is at least 99.8 per cent complete after the addition of 13 per cent zinc (Fig. 11). The decrease in uranium solubility is due to a change from primary UCd_{11} crystallization to U_2Zn_{17}. Also of considerable practical interest in the uranium-cadmium-zinc system is that, in solutions containing more than 4 per cent zinc, not only is the low-temperature uranium solubility markedly reduced but the high-temperature solubility is significantly increased.

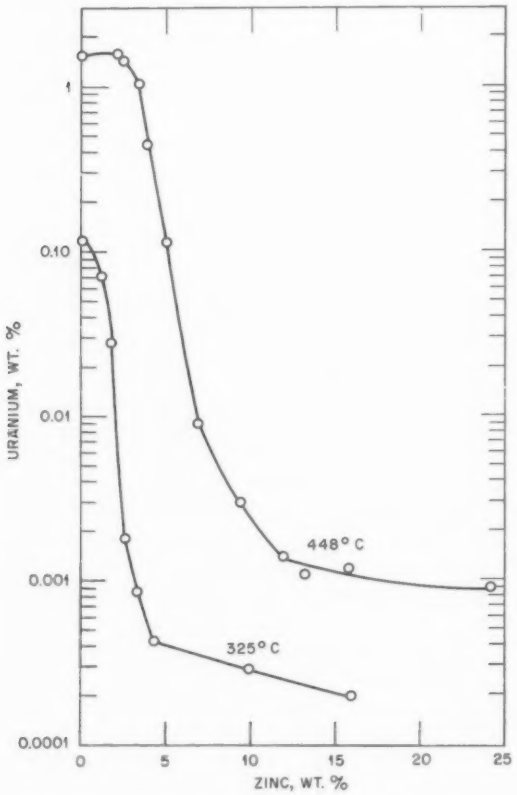

Figure 11—Effect of zinc on the solubility of uranium in cadmium.[39]

The coprecipitation behavior of plutonium with uranium is important process information. The coprecipitation of plutonium from cadmium solutions is the same as that in the zinc system; that is, plutonium coprecipitates with the intermetallic uranium compound but not with uranium metal. The Doerner-Hoskins coprecipitation law is obeyed for coprecipitation of plutonium on UCd_{11}.[39] The coefficient of 0.67 is the same as that found previously for coprecipitation with U_2Zn_{17}.

Precipitation of impurity elements out of metal solution by addition of precipitating elements is another purification mechanism. Addition of zirconium or titanium to bismuth has been found to reduce markedly palladium and ruthenium solubilities, but quantitative relations have not been established.[56]

The extraction behavior of magnesium-silver alloys is under investigation at Ames.[53] The distribution coefficient of cerium at around 1000°C has been found to be very high in favor of the magnesium-silver phase of the order of 10^3 while that of zirconium is less than 10^{-1}. Under somewhat different conditions the coefficient for plutonium was approximately 0.7. Distribution coefficients for other fission products are now being determined.

Operation of a small-scale, semicontinuous graphite extractor and runs made in it for extracting irradiated neodymium from a molten uranium-neodymium alloy using droplets of molten silver at 1250 and 1290°C have been reported.[57] Two different silver drop sizes and flow rates were used. Extraction efficiencies of 15 to 35 per cent were found. Large amounts of neodymium were removed by carbide slagging, indicating the need for a more inert material of construction for the extractor.

Oxide reductions by magnesium or calcium in metal solutions are employed in several processes under consideration for irradiated fuels (both oxide and metallic) and, in addition, may have important applications in raw materials production. A number of sites are investigating oxide reductions, principally those of uranium.

Argonne plans to remove the skull remaining in the crucible after a melt-refining operation by converting it to an easily poured oxide powder.[47] This powder will be subsequently reduced by magnesium in cadmium. Reduction yields have not been quantitative (up to 60 per cent). Ceric (and presumably other rare-earth oxides) are easily reduced by either magnesium or uranium in cadmium solution because of the very low activity coefficients of rare-earth metals in cadmium or zinc solution.[39]

Low-temperature (200 and 300°C) reductions of UO_2 by calcium- or magnesium-mercury amalgams have been tried at Brookhaven with little success.[58] They have found that there exists a problem of a long induction period. Efforts to remedy the situation have been in the direction of producing wettable oxides by various oxide pretreatments.

In a gram-scale test Oak Ridge has reported a 60 per cent reduction yield for uranium dioxide ceramic pellets (fired at 1700°C) when reacted with magnesium in the presence of magnesium chloride at 1000°C in a pressure bomb. Leakage of magnesium was suspected.[16]

Processing of Oxide Fuels

A number of sites are investigating methods for processing and refabricating highly irradiated, short-cooled uranium dioxide fuels.

Work is continuing at Atomics International on processing of uranium oxide fuels by cyclic oxidation-reduction with oxygen and hydrogen to pulverize uranium dioxide pellets.[59] Gaseous fission products are released and some others are volatilized. Experiments were conducted to determine the feasibility of oxidizing "fissia" pellets at temperatures below 375°C. The powder produced by oxidation for 40 hr at 300°C had an average particle size of 2.2 μ. It was concluded that an operating temperature of 375°C gives convenient operating times for laboratory-scale experiments, but for plant-scale operations a temperature near 300°C may be more desirable for producing finer particle size powders.

At Ames, work was continued on the carbon reduction of uranium oxide.[53] This work has the objectives of finding some means or material of containing the molten charge at the elevated temperatures required for the reaction, lowering the carbon content of the product metal, and increasing metal yields. Sintered uranium dioxide crucibles have been used for the reactions. These have worked for just one reduction because of the wetting action of the liquid product. The yields of uranium metal ranged from 70 to 80 per cent, and, although this is low, it is attributed to the volatility of uranium dioxide at the temperature required to get appreciable reduction (>1800°C). It was discovered that uranium metal when heated to 1800°C in an yttrium oxide crucible did not attack the crucible. The crucible was found to have good thermal shock resistance and it is also a good container for melting thorium.

Reduction of oxides by suitable reducing agents in liquid metal has been discussed under the heading Liquid Metal Processes, p. 22

Processing of Thorium-Uranium Fuels

Several recent papers have reviewed methods for decontamination of thorium-uranium fuels. Some of these methods were discussed in a previous Review.[60]

1. Direct volatilization of many fission products in an arc-melting furnace using a nonconsumable tungsten electrode results in removal of the strontium, cesium, and appreciable quantities of the rare earths.[61,62] Consumable arc melting has recently been investigated, but results were generally inferior to the nonconsumable process.[63] However, because it lends itself to ease of operation, it may find use in the fabrication of metal decontaminated by another process.

2. Another possible procedure is drip melting in which a thorium slug is suspended in vacuum in a high-frequency induction coil.[61,64] Power is supplied at a rate such that the metal slowly melts and drips. Vaporization of the fission products occurs at this point. Indications are that the fission-product removal will be similar to that realized by nonconsumable arc melting.

3. A third method providing sizable theoretical decontamination factors is fused salt electrolysis.[61,62] In this process irradiated thorium is dissolved anodically into a molten salt bath along with the more electropositive fission elements. The noble elements do not dissolve but remain as an anode sludge. Thorium is deposited at the cathode, leaving the more electropositive elements in the electrolyte as ions. The fused salt bath consisted of 45 mole % sodium chloride, 45 mole % potassium chloride, and 10 mole % zinc chloride. The zinc chloride was used as a thorium oxidant, thorium replacing zinc in the salt bath in the dissolution process. Molten zinc was used in the cathode department so that a thorium-zinc alloy was formed on deposition of the thorium. Fission-product decontaminations realized were as follows:

	% removed		% removed
Cesium	99.5	Rare earths	85.0
Strontium	99.5	Cerium	79.0
Ruthenium	90.0	Zirconium	60.0

Some vaporization of protactinium occurred which is undesirable. Its volatility is much more than originally estimated. (This is an even more severe problem in the arc and drip melting processes.)

4. Attention is now being given at both Ames and Atomics International to separation by magnesium extraction.[53,54,59] Thorium is highly soluble in magnesium, whereas uranium is highly insoluble. In this process it has been determined that the protactinium is nearly quantitatively extracted from a magnesium–38 per cent thorium phase by molten uranium-chromium. Because the quantity of U^{233} which would be present in any such process is very small, consideration is being given to redissolving the uranium in a fused salt from which fission-product impurities would then be selectively reduced. The uranium would finally be recovered by use of an appropriate reducing agent such as magnesium or magnesium alloy. Accordingly, dissolution studies are in progress in which uranium is dissolved in a potassium chloride–lithium chloride eutectic containing 10 to 20 wt.% zinc chloride. The initial reaction rate is fairly high but the reaction soon subsides and then proceeds slowly, apparently because of the formation of a reaction layer of U_2Zn_{17} on the surface of the uranium.

Fission-product removal from a mixture of potassium, lithium, and uranium chlorides with liquid zinc at 450°C should result in practically complete removal of the noble fission products. Exploratory experiments have indicated that the amount of uranium extracted into the zinc phase from a 3.5 wt.% uranium-salt is less than 100 ppm. Equilibration of the same salt mixture at 500°C with zinc containing 5 to 7 wt.% magnesium reduced the uranium content of the salt to 0.05 wt.%. The behavior of protactinium was essentially identical to that of uranium. Uranium solubilities in a silver–65 per cent magnesium alloy were 1.5 and 2 per cent at 1000 and 1075°C, respectively.[59] This alloy is therefore not a suitable solvent for separating uranium from thorium fuels.

Miscellaneous

The thermal conductivity of the plutonium-iron eutectic mixture was measured in both the solid and liquid states.[65] The thermal conductivity values obtained varied from 0.034 cal/(cm)(sec)(°C) at 220°C to 0.042 at 400°C in the solid state and from 0.043 at 420°C to 0.046 at 520°C in the molten state. The curves appear to be linear with positive temperature coefficients for both phases. Results are accurate to less than ±5 per cent.

An yttrium loop circulating a uranium-chromium eutectic alloy at 1000°C failed because of sagging of the stainless steel.[54] However, there was no evidence of mass transfer or intergranular attack of the yttrium which remained shiny and ductile. These failures indicated stainless steel does not have sufficient strength or resistance to oxidation to serve as a sheath. Inconel is to be tried next. A thorium-magnesium eutectic was circulated at 850°C in a niobium loop for 650 hr. Again, no signs of mass transfer or other attack of the niobium was evident.

Homogeneous Reactor Processing

Reactors utilizing homogeneous fuel have the potential advantage that a side stream of fuel can be continuously removed and processed. Since this processing could conceivably be accomplished in a closed loop, modest decontamination is adequate. The aqueous homogeneous reactor at Oak Ridge is one of the reactors utilizing this concept.

To effect more rapid solids removal from the circulating fuel, a multiple hydroclone assembly has been installed in the HRT chemical pilot plant in addition to the original hydroclone. The multiple assembly consists of thirteen 0.6-in.-diameter hydroclones piped in parallel. The effluent from these units then passes at a rate of 10 gpm to the original single hydroclone system. Preliminary operational data indicate that the new installation is capable of removing solids at a rate three times greater than that of the original installation, about 5.5 g/hr.[4]

Development work on the electrolytic removal of nickel and manganese from circulating fuel solutions is continuing. In bench-scale experiments it was found that removal was more rapid from D_2O solutions than from H_2O. Residual concentrations of the contaminants in the fuel have been consistently below 50 ppm with no mercury contamination being observed. Prior to treatment, the fuel is concentrated to a uranium concentration of about 60 g/liter. Agitation of the mercury cathode was found to be necessary in order for the cathodically deposited

nickel, copper, and manganese to alloy properly with the mercury. Following use, the latter is reconstituted by contacting with nitric acid–peroxide mixtures or sulfuric acid.[4,66]

Corrosion

The selection of materials of construction must of necessity be an integral part of all process development. Where processes involve environments that are unusually corrosive, programs have been set up to determine which materials are most promising. In this section an effort is made to consolidate current information on such processes where programs have been established.

Solvent Extraction

Existing AEC production plants for the processing of reactor fuels are of the solvent-extraction type. Some of the newer fuels cannot be dissolved in the present equipment and by present procedures to produce a feed for processing directly into these plants; as a result, several AEC sites are developing head-end procedures for these fuels that are compatible with the existing plants.

A proposed method for handling stainless-steel matrix fuels is the Darex process. The proposed dissolution environment is 5*M* nitric acid and 2*M* hydrochloric acid. Titanium is generally considered to be the most promising. Most recent corrosion efforts have been directed to studying the behavior of titanium under heat-transfer conditions. In recently completed tests where the metal temperature was 135°C, corrosion rates of 1.5 to 2 mils/month were observed in 2000-hr exposures. In a parallel test in which 0.01*M* stainless steel and 0.004*M* U(VI) were added to the reference solution, rates of less than 1 mil/month were obtained. Some shallow cracking was also noticed.[5]

It was reported in the preceding Review[3] that Hanford was considering Hastelloy F as a possible material of construction for Darex process equipment. Preliminary experiments yielded corrosion rates of 4 and 2 mils/month in liquid and vapor phases. Exposures of a Hastelloy F heat-transfer probe in the Darex pilot-plant dissolver confirmed the low rates of attack obtained in the laboratory. However, severe interface attack ranging in depth to 60 mils was observed during the exposure which was estimated at 250 hr at boiling temperatures and 623 hr at lower temperatures.[67] Laboratory tests further demonstrated that stagnant interfaces are conducive to high local attacks. When solutions were boiled or were sparged with air at room temperature, little interface attack was observed. However, with no boiling and/or without an air sparge, severe attack was found.[11,68]

Haynes-25 alloy was also tested under heat-transfer conditions in Darex dissolvent. Six months exposure in a pilot-plant unit revealed little general corrosion; however, some local attack was noticed in sensitized areas, but no preferential attack was noted at the interface.[68]

In anticipation of possible utilization of Darex wastes for the isolation and recovery of fission products, a series of corrosion tests were made with types 304 ELC and 347 stainless steel in such environments. Boiling solutions of 3*M* nitric acid containing 60 g/liter of dissolved corrosion products served as the reference solution in which chloride contents were varied from 0 to 800 ppm. General attack was less than 5 mils/month; however, severe local attack occurred in sensitized areas.[69]

The Sulfex process can also be used for dissolving or decladding stainless-steel fuels. Several previously untested materials were subjected to Sulfex environments during the past period. Welded and annealed Haynes-25 was found to have corrosion resistance comparable to that of Hastelloy F. However, the presence of dissolved stainless-steel corrosion products caused preferential weld metal attack.[11,68] Metals tested that did not have adequate corrosion resistance in the Sulfex environment included titanium[67] and stainless-steel type 319L.[69]

A topical report on the development of the Sulfex process was published during the past period.[70] Corrosion data included were restricted to those obtained on Carpenter 20. In 32-day exposures in boiling 4*M* and 6*M* sulfuric acid solutions, corrosion rates were 54 and 62 mils/year, respectively. In the presence of 25 and 45 g/liter of dissolved stainless-steel corrosion product, these rates reduced to 23 and 43 mils/year. Pitting and cracking were observed in specimens from all four environments. Data from Battelle indicate that this cracking can be prevented by the presence of this stainless-steel corrosion product and careful heat-treatment.

The reference dissolution environment in the Thorex process is 13*M* nitric acid and 0.04*M*

fluoride. Nionel is considered one of the more promising materials of construction compatible with both Thorex and Sulfex solutions. Current efforts at Oak Ridge are being devoted to the effect of heat-treatment on corrosion.[5,69] Where heat-treatment at 1850 to 1950°F following welding has been done, corrosion was less than 2 mils/month in 1000-hr exposures; no local effects were observed. Where welding followed heat-treatment at 1850°F, the general corrosion was unchanged; however, all welds were pitted and intergranular attack was observed adjacent to welds.

An alternate proposal for the processing of Consolidated Edison fuel is a combination of the Darex and Thorex procedures. The testing of titanium in various Thorex environments has begun. Some of the reported results are shown in Table III-6.[67] In a series of cycling experiments titanium was exposed to 13 Darex-Thorex cycles. Results were encouraging with a measured attack of less than 0.2 mil/month.

Table III-6 CORROSION OF TITANIUM 75A IN THOREX SOLUTIONS[67]

Application: Processing of S.S. clad ThO_2-UO_2 fuel by Darex-Thorex combination
Reference solution: 13*M* HNO_3, 0.04*M* F^-
Temperature: Boiling
Welds: Described as poor

		Butt weld, mils/month		Lap weld, wt. loss, mg*	
Additive	Exposure	24 hr	240 hr	24 hr	240 hr
0.04*M* Al^{+3}	Vapor	4.5	1.3	†	93
	Liquid	0.4	0.9	2	31
0.20*M* Al^{+3}	Vapor	2.3	0.3	†	70
	Liquid	0.0	†	0.1	†
			72 hr		
0.04*M* Th^{+4}	Vapor	8.1	7.0		
	Liquid	1.7	2.9		
0.20*M* Th^{+4}	Vapor	†	0.04		
	Liquid	1.2	0.31		

*Original sample weights: 2.6 to 3.1g.
†Weight gain.

The Niflex process (nitric + hydrofluoric acids) is a third method by which stainless-steel matrix fuels can be dissolved or declad. In a series of bench-scale tests Hastelloy F welds were tested as a function of heat-treatment. The exposure was to boiling 1*M* nitric acid−1*M* hydrofluoric acid. Samples were heat-treated for 1 hr at 2100°F and water-quenched. A second heat-treatment for 1 hr at temperatures varying from 1400 to 1900°F followed. The second heat-treatment was detrimental to the corrosion resistance; severe intergranular attack was observed, especially when the second heat-treatment was at a temperature of 1600 to 1700°F.[11,68]

Aqueous methods of processing zirconium matrix fuels include Zircex and Zirflex. In the latter process the fuel is dissolved in 3*M* NH_4HF_2 or 6*M* NH_4F−1*M* NH_4NO_3. A series of scouting tests were made in the latter environment at refluxing temperatures.[69] The results are shown in Table III-7.

A topical report on the corrosion studies in the Oak Ridge Thorex pilot plant was recently released.[71] Several process vessels were monitored by the insertion of both stressed and unstressed, welded and unwelded, specimens. These included the dissolver, the feed adjustment tank, a catch tank, and a vapor separator. Typical results are shown in Tables III-8 and III-9. The behavior of stainless-steel type 304L was quite comparable to that of type 309 SCb (low carbon, columbium stabilized). Preferential attack was restricted to some heat affected zones adjacent to weld deposits, and these were not consistent in their occurrence. No stress corrosion cracking was observed nor was severe crevice corrosion noticed. Areas of highest corrosion included the vapor phase of the feed adjustment tank and the evaporator system. In some instances rates of up to 47 mils/year were observed. It was estimated by the author that the life of the vapor phase of the feed adjustment tank is about four years.

Volatility Processing

A potential method for the processing of zirconium-base fuels is the fused salt volatility process. The fuel is converted to its respective uranium and zirconium fluorides by dissolution in a molten fluoride environment through which anhydrous hydrogen fluoride is passed. The solubilized uranium tetrafluoride is converted to the volatile uranium hexafluoride by passing fluorine through the melt. Separation of the uranium hexafluoride from fission-product fluorides is accomplished by distillation or adsorption on sodium fluoride traps.

Battelle has completed a study for ORNL of potential materials of construction for the first step of the process, i.e., for the hydrofluori-

Table III-7 RESULTS OF SCOUTING EXPERIMENTS IN BOILING ZIRFLEX SOLUTIONS[69]

Exposure: Liquid phase. (In all cases interface and vapor phase corrosion was less.)

Metal	Welded	Corrosion rate, mils/month			
		Cycle I*		Cycle II†	
		24 hr	72 hr	24 hr	72 hr
Haynes-21	No	2.8	2.3	3.3	2.8
Haynes-25	No	12		6.9	
309 Cb	Yes	8.6	8.5	3.7	3.4
309 Cb	No	7.8	7.2	3.3	2.4
316	Yes	18	15	4.4	4.0
319L	Yes	29	27	5.5	5.1
Hastelloy F	No	19	15	13	7.2
Titanium 75A	No	419		2.5	
Nionel‡	Yes	12	12		

*6*M* NH_4F, 1*M* NH_4NO_3.
†10*M* H^+, 10*M* NO_3^-, 0.05*M* F^-.
‡Data taken from reference 5.

Table III-8 CORROSION OF 304L AND 309 SCb IN THOREX PILOT PLANT (ORNL) DURING PRODUCTION PERIOD[71]

Solution compositions: See Table III-9

Location	Corrosion, mils/yr		Comments
	Type 309 SCb	Type 304L	
Dissolver, liquid	3.1 ± 0.5	8 ± 0.4	Uniform corrosion; no intergranular attack; some edge attack; welds OK.
Dissolver, vapor	2.0 ± 0.3	3.6 ± 1.7	Uniform corrosion; some knife line attack; no intergranular attack.
Feed adjustment tank, liquid	6 ± 2.5	4.2 ± 0.4	Localized edge attack; some knife line attack in 309.
Tank, vapor	35 ± 8.5	21.1 ± 2.0	Grain boundary attack; surface roughening; intergranular edge attack.
Evaporator system		10.5 ± 3.7	Edge corrosion with pitting; welds OK.

Table III-9 TYPICAL LIQUID COMPOSITIONS IN THOREX PILOT PLANT UNITS[71]

Constituent	Composition, mole/liter					
	Dissolver		Feed adjustment tank		Evaporator system	
	Initial	Final	Initial	Final	Initial	Final
HNO_3	13.0	5.0	5.0	0.5	0.2	1.5
$Th(NO_3)_4$	0	1.0	1.0	4.0	0.025	2.0
$Al(NO_3)_3$	0.04	0.37	0.37	1.6		
$Hg(NO_3)_2$	0.04	0.015	0.001	0.004		
Fluoride	0.003	0.001	0.015	0.047	0.004	0.009
Temp., °C	110	110	110 to 155		110 to 115	

Table III-10 CORROSION OF NICKEL-MOLYBDENUM ALLOYS IN HYDROFLUORINATION ENVIRONMENT OF FLUORIDE VOLATILITY PROCESS[72]

Melt: $NaF-ZrF_4$ or NaF-LiF as indicated
HF rate: 10 g/hr unless noted

Run	Melt*	Temp., °C	Time, hr	H_2 addition†	Corrosion, mils/month: Wt. change (dimensional change) INOR-1	Wt. change (dimensional change) INOR-8	Metallography (intergranular attack) INOR-1	Metallography (intergranular attack) INOR-8
Liquid Phase Corrosion								
17	$NaF-ZrF_4$, B	650	500	No	2.5	0.6		
17A‡	$NaF-ZrF_4$, M	650	500	No	8	4.5		
19	$NaF-ZrF_4$, M	650	425	Yes	2	0.4		
19A	$NaF-ZrF_4$, M	650	480	No	4	6		
19B	$NaF-ZrF_4$, M	650	200	No				
19C	$NaF-ZrF_4$, M	700	200	No	17	17		
22	$NaF-ZrF_4$, F	650	200	Yes	0.6	0.8		
22A	$NaF-ZrF_4$, F	650	200	No	5	4		
20	NaF-LiF, B	700	260	No	17	20		28
21	NaF-LiF, B	700	120	Yes		30		
24	NaF-LiF, B	700	90	No	38	43		
23	NaF-LiF, F	600	200	No	1.7	2.5		
23A	NaF-LiF, F	650	200	No	4.4	4.2		
23B	NaF-LiF, F	700	160	No	11	15		

Interface Corrosion

Run	Corrosion, mils/month: Micrometer measurement (dimensional change) INOR-1	INOR-8	Hastelloy B	Metallography (intergranular attack) INOR-1	INOR-8	Hastelloy B
17	9	16	9	15	23	12
17A	16	45				
19				2.2	0.9	
19A	7	14				
19B	38	21	6			
22A	4	4	5			
20					28	
24				120	100	
23B	22	20	15			

*$NaF-ZrF_4$: B, Beginning composition (mole %): 62 NaF–38 ZrF_4
M, Middle composition (mole %): 50 NaF–50 ZrF_4
F, Final composition (mole %): 43.5 NaF–56.4 ZrF_4–0.11 UF_4
NaF-LiF: B, Beginning composition (mole %): 43 NaF–57 LiF
F, Final composition (mole %): 19.3 NaF–25.6 LiF–54.9 ZrF_4–0.21 UF_4
†Hydrogen addition, 0.24 g/hr.
‡HF rate, 25 g/hr.

nator.[72] Nickel-molybdenum alloys were found to be markedly superior to other materials tested. Those having serious deficiencies include Inconel, "A" nickel, copper, Monel, and silver. The most consistent disadvantage of the rejected materials was their sensitivity to some form of subsurface attack. For example, nickel was found to be extremely sensitive to trace sulfur constituents while Inconel was rejected because of preferential leaching of the chromium. The point of greatest attack on both melt compositions examined (sodium fluoride–zirconium fluoride, sodium fluoride–lithium fluoride) was the interface region. The sensitivity at this location plus corrosion in the liquid phase was found to be markedly reduced by additions of hydrogen to the incoming hydrogen fluoride and by the presence of dissolving zirconium. Increasing temperatures accelerated the corrosion. A comparison of selected

results for three nickel-molybdenum alloys is shown in Table III-10. INOR-8 was selected as the most satisfactory compromise material. The INOR alloys were developed by the Metallurgy Division of ORNL and the International Nickel Company. "L" nickel has been considered the most promising material available for the fluorination step. In sodium fluoride–zirconium fluoride melts at 600°C, nickel is subjected to an intergranular attack which, although not as severe as in the hydrofluorination environment, still constitutes its most serious limitation. Recent tests have been made to determine the effect of fluorine purification and lower operating temperatures on the degree of intergranular attack. The results are shown in Fig. 12. The most pronounced effect occurred at the interface. Fluorine purification did not reduce the dimensional change to any great extent but did reduce markedly the intergranular attack. The lower operating temperature reduced both. It will be noted that interface effects disappeared at 475°C.[38]

At ANL efforts are being made to bypass the corrosion problem in the fused salt process by the use of a frozen wall technique. The metal container which serves as a structural support is cooled forming a layer of solidified salt on the metal proper. Heat is introduced centrally into the molten melt by either one of two techniques: induction heating or the use of easily replaceable resistance heaters. Both techniques appear to have promise.[38]

Pyrometallurgical Processing

Pyrometallurgical processing has the potential economic advantage of not requiring a change in physical phase. Materials of construction problems are severe—the containment of molten plutonium and uranium is difficult.

The testing of materials of construction for the LAMPRE reactor at Los Alamos provides information for molten plutonium environments.[73,74] It had been reported earlier that tantalum has the promise of being a useful material, but its behavior is markedly influenced by the purity of the metal and the degree of cold work. More recent studies suggest that, in addition, the purity of the molten metal environment is important. It was found, for instance, that when the plutonium-iron alloy used in the test was prepared from cast iron, corrosion rates were considerably less than when the al-

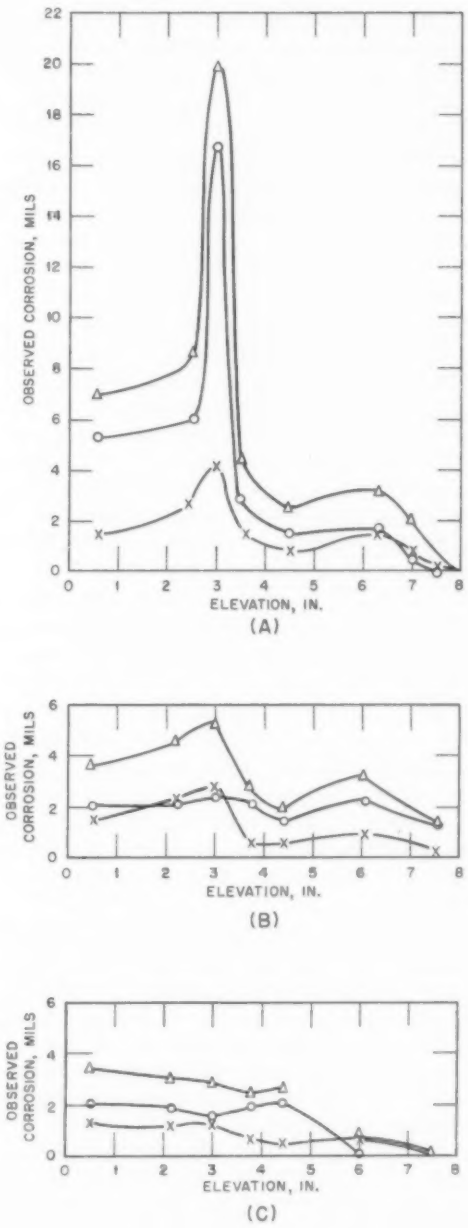

Figure 12—Effect of fluorine purification and temperature on corrosion of "L" nickel in fluorinated fused fluoride melts.[38] X, dimensional; O, intergranular; Δ, total. (A), 63 hr fluorine sparge; 153 hr helium sparge; 10 g/hr fluorine, 600°C; equimolar $NaF-ZrF_4$. (B), 10 g/hr fluorine, 600°C; equimolar $NaF-ZrF_4$; purified F_2 (NaF trap). (C) 10 g/hr fluorine, 475°C; 37 mole % NaF; 26 mole % LiF; 37 mole % ZrF_4.

loy was prepared from high-purity steel. Pure fuel corroded tantalum at 700°C at a rate greater than 10 mils/year while the same material containing a carbon addition corroded at the rate of 0.25 mil/year. Additions of silicon and manganese were not found to be helpful. It has been suggested that the role of carbon in decreasing the rate of attack is the formation of a protective tantalum carbide film. Presumably some minimum carbon content is required to yield a film that is self-healing.

Small bench-scale studies are being made at Los Alamos to determine the rate of reaction between molten plutonium and a number of refractory oxides at temperatures of 1000 to 1650°C. Above 1400°C, MgO, CaO, and CeO_2 were found to have reaction rates in excess of 500 mg Pu/(sq cm)(hr). At 1500°C, ThO2, La_2O_3, and Y_2O_3 had reaction rates of less than 10 mg Pu/(sq cm)(hr). Yttria and possibly thoria possess good resistance at 1650°C.[74]

At ANL experiments are being conducted in molten zinc and cadmium-base environments at temperatures of 750°C and 550°C, respectively.[38,39] Materials that have been rejected for the zinc environment include Colmonoy-6 coated steel, titanium, and vitallium. Unlike these metals, tantalum did not dissolve in zinc but was appreciably attacked. Tungsten and molybdenum were the only materials tested which show some promise. Additions of 46 wt.% magnesium to the zinc reduces but does not eliminate corrosion.

Mild steels, both high and low carbon, stainless-steel type 410, and tantalum have been found to have excellent resistance in cadmium-magnesium-uranium melts at 550°C. No iron has been found spectrographically after 100-hr exposures in the melt. Stainless steels (300 series) are subjected to preferential attack of the nickel. In additional tests in which 2, 4, 8, and 10 wt.% zinc were added to a cadmium-magnesium melt, no corrosion was observed in mild steel alloys. Evidently zinc contents up to 10 per cent can be tolerated.[38,39]

Miscellaneous Corrosion

A fluidized-bed technique for the calcination of Redox type process wastes is under investigation at ANL and Idaho. The present practice in an ANL pilot-plant unit includes filtering of the waste gases through sintered stainless-steel type 316 filters. A number of corrosion tests have been made to determine under what conditions simulated off-gases corrode these filters. In a series of tests, 3*M* nitric acid was vaporized into either nitrogen or air. Tests were made at 550°C, and during 100 hr of such exposure general attack was observed through the entire cross section of sintered metal.[38]

At the Idaho Chemical Processing Plant, studies are also being made on the calcining of Redox type wastes. Procedures there include the use of wire mesh for the adsorption of radioactive ruthenium from off-gases. Stainless-steel type 304 mesh was exposed for 26 days at temperatures of 550°C. The weight gain of the mesh was 0.104 wt.%. This is considered very low for the particular application.[75]

A topical report on the evaluation of materials of construction for anodes in the Flurex process was recently published.[76] The Flurex process is described as an electrodialytic procedure for converting aqueous uranyl nitrate to U(IV) fluoride salts of the general formula MUF_5. In the process an alkaline ammonium or sodium nitrate solution is used in the anode compartment. Materials tested included 300-series stainless steels, nickel alloys, platinum, tantalum, Zircaloy-3, gold, and carbon. These were tested at room temperature in 0.1*M* ammonium nitrate and 0.0003*M* ammonium fluoride at anode current densities of 1 amp/sq in. The corrosion rates were reported as mg/(amp)(hr). The corrosion of 18-8 stainless steels typified by S.S.-347, S.S.-304L, and S.S.-316L ranged up to 4.4 mg/(amp)(hr). Higher stainless alloys as S.S.-309, S.S.-312, and Carpenter 20 corroded at rates in excess of 400 mg/(amp)(hr). Nickel alloys were intermediate in their corrosion behavior while platinum had the lowest attack, the rates being on the order of 6 and 0.02 mg/(amp)(hr), respectively.

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Operating Experience

A comprehensive report of waste-disposal problems associated with uranium mills was issued during the quarter.[1] A number of methods for removing radium from the mill effluents were discussed including various precipitating agents, ion exchange, and percolation through barite.

An incident which occurred at Hanford in June 1958 has been described in an unclassified report.[2] Instability of the steel liner in the bottom of a storage tank was indicated by column rod readings through the risers in the top of the tank. These measurements showed an upward dishing of the tank bottom to a height of about 4 ft, followed by a return of the liner to a horizontal position within a month. A number of possible explanations for the incident are discussed in detail.

Reduction to Solids

The adsorption of activity onto clays, its incorporation into glass, and two methods of calcining liquid wastes are discussed.

Adsorption on Natural Materials

A method of solidification of radioactive liquid wastes used at UCRL consists of adding Portland cement and mixed and expanded vermiculite to the waste until all liquid is adsorbed. The solidified waste is handled and stored as a solid waste package.[3]

BNL reports that the efficiency of clay columns for the decontamination of high-level wastes is dependent on the concentration of nonradioactive cations present in the influent solutions.[4] Concentrations of corrosion products in expected wastes have been estimated to be 0.005*M* iron, 0.0008*M* chromium, and 0.0009*M* nickel. These concentrations, although low, are sufficient to interfere with the efficient uptake of fission products on clay. One of the better methods of eliminating the undesirable cations is precipitation with sulfide. The precipitation step leaves a residue contaminated with fission products. The use of thioacetamide instead of hydrogen sulfide produces a coarser precipitate which has less scavenging effect.

A waste solution that has been concentrated, deacidified, and then treated with thioacetamide yields a solution which should be compatible with the clay process and would be expected to yield high decontamination factors for strontium and cesium. A series of runs in 5-ft clay columns with iron concentrations ranging from 0.001*M* to 0.00001*M* indicate that concentrations of iron greater than $10^{-4}M$ cannot be tolerated for efficient clay absorption. At the present time the clay process consists of the following steps:

1. Evaporation under vacuum to remove nitric acid.
2. Reduction of the residual nitric acid with formaldehyde.
3. Dilution and pH adjustment.
4. Sulfide precipitation of the corrosion products.
5. Adsorption and fixation of fission products in clay.

In England a series of glasses incorporating wastes have been studied.[5] The composition ranges expressed in terms of the constituent oxides are as follows:

Oxide	Wt.%
SrO	2.7–25.0
Na_2O	15.8–26.2
B_2O_3	3.5–15.0
Al_2O_3	0–13.6
SiO_2	40.0–62.8
TiO_2	0–23.1

In addition, some glasses contained NaF as a flux in proportions varying from 4.2 to 8.5 wt.%.

It is possible to prepare glasses containing an appreciable proportion of strontium which show good resistance toward leaching by water, alkali, and chromic acid and also toward dilute acids after initial treatment. The marked reduction in leaching rate after the initial stages,

together with the absorption of activity from solution if the treatment is sufficiently prolonged, suggests the possibility of using an active glaze (1) covered with a thin coating of inactive glaze of similar composition and (2) given a preliminary acid treatment to stabilize the surface. Greater resistance toward leaching may be attained by careful choice of the proportions of alkali and borate flux, which also enables higher strontium contents to be achieved. The introduction of TiO_2 also serves to increase resistance, without raising the temperature of fusion as much as does the addition of Al_2O_3. Satisfactory glasses have been prepared containing up to 25 per cent of SrO by fusion at ~1100°C; higher percentages of SrO (30 to 60 per cent) have been incorporated into unfluxed aluminosilicate and silicate glasses, but these require temperatures of ~1400°C for fusion.

A test has been started to measure the dispersal of radioactivity from glass containing fission products when buried in wet ground.[6] This test should also permit a comparison of the leaching rates obtained in the laboratory with those obtained in the field and should demonstrate the degree of reliability with which laboratory results may be extrapolated. More than 300 curies of mixed fission products have been incorporated into blocks weighing 2 kg each. Measurements made in the laboratory indicate that the leaching rate of this glass decreased during the first three weeks of submersion in distilled water by a factor of 500 to a level of 1.0×10^{-7} g/(sq cm)(day).

Calcination

The Hanford 8-in. radiant heat calciner[7,8] has been used to process neutralized Purex waste which results in slurries of 7*M* sodium nitrate containing a suspension of the hydrous oxides of iron, aluminum, chromium, and nickel.[9] No difficulty was encountered in pumping or atomizing the slurry, but the sodium nitrate coated the walls of the calciner and eventually terminated the operation. Small-scale experiments were carried out to test several ways of destroying nitrate chemically. Addition of sugar was found to work best. A mixture of simulated neutralized waste and sugar was stable for days at 80°C but reacted readily at 220°C. A run was accordingly made in the 8-in. unit with a slurry feed containing 250 g/liter sugar. Operation was smooth, and there was little or no build-up of dust on the walls. The product powder (predominantly sodium carbonate) had a bulk density of 0.85 g/cc and fused at 860°C to compact glassy melt with a density of a 2.3 g/cc. Residual nitrate was low (<0.0015 per cent).

An earlier run on high acid feed indicated that some caution must be exercised in the use of sugar to avoid prereaction in the feed tank.[10] One minor, but potentially grave, incident resulted from this reaction. On standing overnight after sugar addition, a high acid feed underwent reaction and ruptured the plastic feed lines.

At Argonne, feasibility studies are being performed on the fluidized-bed calcination of Hanford Purex low acid waste solution.[11] Results covering about 200 hr of operation are quite promising. A granular free-flowing product has resulted from calcining operations performed at 500°C. Some difficulty has been experienced in the operation due to atomizing nozzle lump formation, some particle agglomerization, and particle growth. These problems are being solved by the application of new nozzle designs, the addition of sugar to the feed, and the use of attrition air.

At Idaho, initial tests have commenced on a NaK-heated 100 liter/hr pilot-plant aluminum nitrate fluid-bed calciner.[12] In the smaller pilot-plant unit, increasing feed spray air ratio was found to increase particle loading in the cyclone effluent. Laboratory studies indicated that a venturi scrubber using dilute nitric acid at 80°C should remove ruthenium effectively from calciner off-gas. In a pilot-plant test in which a significant fraction of ruthenium feed was retained by the alumina, substantial absorption of volatilized ruthenium was obtained. Thermal conductivity of alumina near 3000°F was about 0.26 Btu/(hr)(ft)(°F). In leaching studies very little strontium or plutonium was removed by water from alumina calcined at 550°C. Dilute nitric acid, however, extracted strontium from this material to the same degree (~50 per cent) as from material calcined at 400°C.

While the 2- by 2-ft calciner at the Chemical Engineering Laboratory (Idaho) was partially dismantled, a visual examination of the exterior of the Carpenter 20 heat-exchanger tubes was made. The tubes were tarnished but showed no evidence of corrosion. This substantiates data from the corrosion test calciner.[13]

The adsorption of ruthenium tetroxide on silica gel and other adsorbents from a vapor phase of air–nitric acid–water has been studied to provide design data for a ruthenium adsorber.[14] Silica gel is used at slightly above the vapor dew point temperature to remove ruthenium from the off-gas. Decontamination factors of about 1000 are experienced. After saturation of the gel, the ruthenium is removed by washing with a small volume of water, and the gel is regenerated by heating in a stream of dry air. Capacities of about 10 g of ruthenium per cubic foot of adsorber have been obtained. This is about 2000 curies per cubic foot with one-year-cooled fission products. Four cycles have been run on the same batch of adsorbent with uniform ruthenium retentions after water washing of about 10 per cent of the total loading.

Final Disposal Methods

The Coast and Geodetic Survey and the AEC announced that a study of simulated radioactive waste packages in the sea will be conducted during the summer of 1959 by skin divers in 50 ft of water off the coast of Martha's Vineyard, Mass.[15] Waste containers will be filled with a colored dye to determine if the packages leak. The skin divers, using underwater color cameras, will photograph the containers as they descend. The dye studies are part of a larger project planned to find out what happens to radioactive waste at sea, involving radioactivity counting in about 25 possible dumping sites, including a disposal area about 20 miles off Boston harbor where wastes of low radioactivity have been dumped in the past.

It was also reported last month that the United States is to be among 15 nations which will participate in a survey, scheduled for 1960 and 1961, of the Indian Ocean to locate the best possible sites for the disposal of radioactive wastes.[15]

A special committee of the National Academy of Sciences, under the chairmanship of Dr. Donald W. Pritchard of Johns Hopkins University, concluded in a report issued in July that a fleet of 300 nuclear-powered surface ships, which might be in operation by 1975, could safely dispose into the ocean low-level radioactive wastes incident to normal operation "without undue hazard to human health."[16] The wastes involved would consist in part of the residues in the ion-exchange resins which filter out radioactive impurities in the reactor coolant. The committee recommended extreme care in discharging wastes in coastal waters and harbors and recommended an international monitoring program and other safety procedures to control radioactive waste disposal at sea.

Removal of Specific Isotopes

A series of scouting experiments are being performed to determine the potential of solvent extraction for waste treatment of fission-product recovery applications. Two extractants have been used to date: 2 per cent di-2-ethylhexyl phosphoric acid (D2EHPA) in Amsco and 4 per cent tall oil in chloroform. Extraction of gross beta activity from synthetic first-cycle aqueous waste spiked with plant waste was studied as a function of pH. Extraction ranged to a maximum of 42 per cent at pH 7.2 with D2EHPA and of 63 per cent at pH 10.3 with tall oil.

In processing waste gas streams from nuclear fuel plants for recovery of the noble gases, nitrous oxide must first be removed. A catalyst consisting of 0.5 per cent rhodium supported on ⅛-in. alumina pellets has been found capable of decomposing nitrous oxide in simulated waste gas streams at catalyst temperatures ranging from 343 to 413°C, when gas space velocities range from 525 to 2220 scf/(hr)(cu ft of packed catalyst vol.).[17] Hydrogen in concentrations up to 2.3 vol.% N_2O, 1.6 to 2.3 per cent H_2, and 13.3 to 17.8 per cent O_2, the remainder being N_2, were reduced by the catalyst to gases containing less than 100 ppm N_2O and no H_2. Less than 50 ppm NO was found in the effluent gas. The presence of higher oxides of nitrogen and acetylene does not decrease the activity of the catalyst.

A recovery process for cerium and promethium which is being studied includes the following steps: (1) isolation of a crude rare-earth mixture from Purex waste, (2) removal of cerium from the rare-earth mixture, and (3) separation of promethium from the other rare earths.[10] The first step is a sulfate precipitation from diluted waste; separation of cerium from the other rare earths is accomplished by oxidation with permanganate and precipitation as the iodate. Following removal of the cerium, the promethium is separated

from the other rare earths and purified by a variation of the Ames cation-exchange resin–EDTA method. By using samarium as a stand-in for promethium and tracing with Pm^{147}, recoveries of 96 to 97 per cent were routinely obtained with a procedure (Step 1) which involved diluting the waste twofold to reduce the iron concentration to 0.25*M*, butting the sulfate to 1*M*, neutralizing to pH 1 with caustic, and digesting at 90°C for at least 1 hr. The crystalline precipitate settled readily and centrifuged to a slurry volume of about 1 per cent. Decontamination factors from ruthenium, cesium, and zirconium-niobium were 1100, 75, and 150, respectively.[9,18]

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Uranium Ore Concentrates

Certain of the ore concentrates received at uranium refineries contain a considerable quantity (1 to 2 per cent) of uranium that cannot be dissolved in nitric acid. This insoluble uranium cannot be extracted by the TBP solvent and is lost from the process in the waste. It has been shown that allowing the material to react with a reducing agent such as carbon monoxide or hydrogen at a temperature of 1240 to 1350°F reduces the insoluble uranium.[1] One source of readily available hydrogen and carbon monoxide is the product of incomplete combustion of propane gas. At Mallinckrodt Chemical Works (Weldon Spring, Mo.) a Herreshoff calcining furnace equipped with propane burners was successfully utilized to achieve a reduction in the nitric acid–insoluble uranium content to 0.1 to 0.2 per cent by reaction with the gases generated by combustion of the propane with 60 per cent theoretical air. The temperature of the powder was maintained at 1200 to 1240°F because overheating produced lumps that were not completely reduced and, in some cases, caused plugging of the hearths. Rates of the order of 500 to 600 lb per hour were achieved in a 13.5-ft-diameter 7-hearth furnace. Digestion of the calciner product in the refinery was no problem. The incremental cost of the operation was calculated to be $0.015 per pound of concentrate. The value of the uranium recovered exceeded the incremental operating cost by a factor of 7. It is contemplated that highly insoluble uranium feeds will be processed intermittently through the calciner.

Uranium Oxides

Fluidized-bed Production

Investigation of a fluid-bed process[2] for the production of uranium trioxide by denitration of uranyl nitrate has been under way at Mallinckrodt Chemical Works for about 21 months.[3] The process involves continuously atomizing uranyl nitrate solution into a heated fluidized bed of uranium trioxide particles, where evaporation and thermal decomposition occur. A sketch of the 10-in.-diameter denitration reactor is shown in Fig. 13. The fluidized uranium trioxide powder is heated by 30, 1-in.-diameter, vertical bayonet heaters through

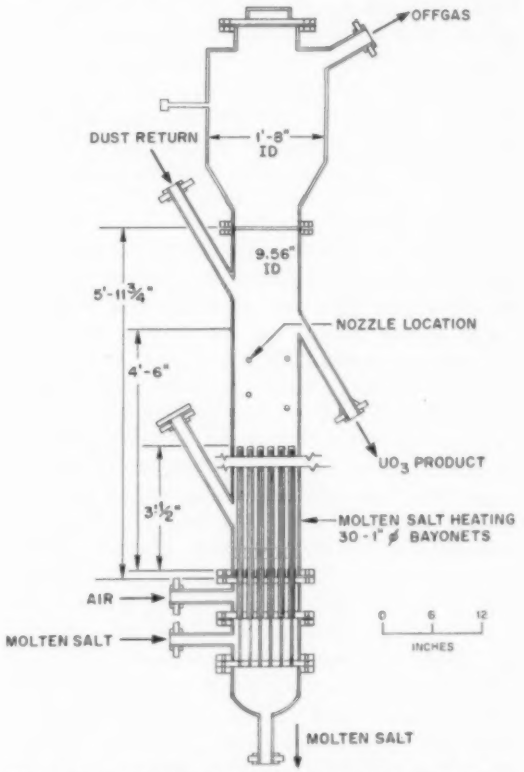

Figure 13—Fluid-bed denitration reactor. (Barbara Elliott, ed., Process Development Quarterly Report. Part II—Pilot Plant Work, MCW-1421, Nov. 1, 1958, p. 70, Confidential AEC report.)

which a molten salt is circulated. Feed liquor is pumped through a heated recycle loop, from which it is metered to a spray nozzle at one of four possible locations. The off-gases leave the reactor at the top and pass through a cyclone separator to a Venturi scrubber. Dust removed by the cyclone falls into a hopper, from which it is returned to the reactor through a rotary valve. The uranium trioxide product overflows from the reactor through a 2-in. downcomer located 4½ ft above the air distribution plate.

The fluid-bed denitrator has been operated at rates up to 500 lb UO_3/(hr)(sq ft of cross section), utilizing concentrated uranyl nitrate feed solutions up to 11.8 lb of uranium per gallon, with satisfactory particle size control. This feed solution was considerably more concentrated than molten uranyl nitrate hexahydrate (9.75 lb of uranium per gallon), and there was no reason to believe that higher feed concentrations could not be employed if suitable pumping and metering equipment were installed. The high production rate achieved has greatly broadened the previously conceived limitations placed on fluid-bed denitration equipment. The fact that this rate was achieved with only one spray nozzle means that the limiting feed rate for a single nozzle is still unknown.

Heat-transfer film coefficients from heater surface to the bed ranged from 37 to 47 Btu/(hr)(sq ft)(°F/ft). Only minor operating problems have been encountered in recent runs. Most of these have been due to plugging in the system that refeeds dust from the cyclones back into the denitrator. A filter system using sintered metallic elements is being designed for installation in the top of the reactor.

Investigation of primary operating variables and their effects has been carried out, and correlations have been developed. Higher feed rates and/or feed concentrations resulted in decreased bulk density (from 4.2 to 3.4 g/cc), due apparently to increased voidage within the particles. Particle size distribution did not change significantly with production rate. Higher bed temperatures and feed concentrations resulted in particles of larger diameter.

The uranium trioxide produced in the denitrator is intended to be processed to uranium dioxide and uranium tetrafluoride in tapered fluid-bed reactors. A pilot-scale fluid-bed reduction reactor employing an internal tapered mandrel has been installed and briefly tested.[4] The tapered mandrel is used to provide a constant superficial gas velocity throughout any vertical plane in the reactor bed. By virtue of the constant velocity, provided the velocity is not too far above that required for incipient fluidization, it is believed that a close approach to "piston flow" of the solids can be achieved. Yet, since the particles are fluidized, the advantages of a fluid bed, particularly the asset of good heat transfer, can still be maintained. A given production rate can be achieved in one piston flow reactor, whereas several stages might be required if conventional, well-mixed fluid beds were employed.

Ceramic-grade Uranium Dioxide

Uranium dioxide offers great promise as a nuclear fuel for use in power reactors. For this purpose the broad requirements are that the uranium dioxide powder should sinter reproducibly, without excessive shrinkage, to a high density, usually greater than 10 g/cc. The starting material for the preparation of ceramic fuel-grade uranium dioxide has been ammonium diuranate (ADU) because the uranium dioxide produced from ADU can be sintered to high density. However, unless the ADU is prepared under carefully controlled conditions, the dioxide is not always as sinterable as desired. Therefore empirical studies of processing variables in the production of uranium dioxide from ADU have been carried out by Canadian workers.[5]

Experimental precipitations of ADU using 300-g batches of uranium showed that the precipitation conditions affect the sinterability of the uranium dioxide powder produced. The conditions found to yield a readily filterable ADU which would reduce to a readily sinterable dioxide were low uranium concentration, high ammonia concentration, relatively fast ammonia addition, high temperature, and high final pH. Rigid control of precipitation conditions is not necessary. Wide control limits apply for precipitation with ammonium hydroxide, whereas for precipitation with gaseous ammonia almost all conditions give a highly sinterable powder. The ADU precipitate with gaseous ammonia yields uranium dioxide of finer particle size. This dioxide must be sintered at a slower rate to avoid cracking while sintering. The addition of 200 ppm of metal oxides (representing impurities) at the metal oxide stage and of large amounts of fluoride at the precipitation stage

has little or no effect on the sintered density of the dioxide.

The following precipitation conditions were recommended, taking into consideration convenience in operation and the trends shown by the experiments to produce a highly sinterable oxide: uranium concentration, 100 to 200 g/liter; ammonium hydroxide concentration, 13*N* (28%); temperature, 60°C; time of precipitation, less than 1 hr; and final pH, 9 to 9.3. These conditions have been used in production work at the Port Hope, Ontario, plant. The ADU produced has consistently yielded uranium dioxide which sinters readily to a density greater than 10.4 g/cc.

Further experiments[6] were carried out to determine the optimum conditions for the continuous (as opposed to batch) precipitation of ADU. With uranyl nitrate solutions at a concentration of 100 g of uranium per liter and aqueous ammonia as reactants, ammonium diuranate precipitated at 60°C at pH above 6.8 consistently yielded uranium dioxide which could be sintered to a density of 10.3 to 10.7 g/cc. As the precipitation pH was increased above 6.8, the ADU became more difficult to filter. Considering both the ease of filtration of the ADU and the sinterability of the uranium dioxide, it is desirable to precipitate the ADU at a pH between 7.0 and 7.5. Variations in ammonia concentration between 5.9*M* and 13.1*M* and uranyl nitrate flow rate between 75 and 167 ml/min (1-liter precipitation tank) did not significantly affect the results.

Another study[7] was carried out to define the effect of reduction conditions on the sintered density of the uranium dioxide compacts. Seven variables which might be expected to affect the properties of the uranium dioxide were investigated. It was found that with ammonium diuranate prepared by the batch procedure recommended above, the reduction conditions could be varied within wide limits without affecting the sintered density of the uranium dioxide. A sample of ADU prepared under somewhat different conditions from the above was more sensitive to changes in reduction conditions.

The conditions which allowed the production of uranium dioxide having the highest sintered density are as follows: the ADU was heated in a hydrogen atmosphere in 1-in.-deep beds at the rate of 200°C per hour to a temperature of 900°C, held at that temperature for 1 hr, then cooled to room temperature. Further handling was done in air.

Within the ranges studied the effects of rate of increase of temperature, the maximum reduction temperature, and the time at maximum temperature were small. Increased depth of the ADU charge decreased the sinterability of the dioxide. When reduced in 1-in.-deep beds the uranium dioxide yielded compacts of density 10.6 g/cc, but when the same material was reduced in 6-in.-deep beds the sintered density was 9.5 g/cc. Heating at 600°C in an inert atmosphere prior to reduction also caused a lowering of the sintered density by as much as 18 per cent.

Since the diameter of the sintered compact is critical for reactor fuel, the reproducibility of shrinkage is of great importance from a manufacturing point of view. The decrease in diameter during sintering of uranium dioxide made by the standard reduction conditions ranged from about 20 to 22 per cent.

Conversion of Uranium Hexafluoride to Uranium Dioxide

Because of the increased interest in uranium dioxide as a nuclear fuel, a more economical process for large-scale production of enriched uranium dioxide is needed. The conventional process includes hydrolysis of the hexafluoride with water, precipitation of ammonium diuranate, calcination, and reduction with hydrogen. At ANL a bench-scale study has successfully demonstrated the one-step, continuous conversion of uranium hexafluoride to uranium dioxide.[8] Hydrogen and steam were used for simultaneous reduction and pyrohydrolysis reactions at 600°C in a 1½-in.-diameter reactor containing a fluidized bed of uranium dioxide. Uranium hexafluoride vapor was continuously fed into the bed, which was fluidized with a preheated steam-hydrogen mixture (mole ratio 2:1). The hexafluoride feed entered through an open quarter-inch tube extending into the fluidized bed.

Good conversion (97.5 to 99 per cent) to uranium dioxide was achieved at feed rates equivalent to about 50 lb uranium/(hr)(cu ft of static bed volume), using 300 to 600 per cent excesses of steam and hydrogen. The dioxide formed as a dense coating on the surface of

the fluidized particles. Residual fluoride content was as low as 0.08 per cent. Negligible amounts of uranium were found in the off-gas condensate.

Bulk densities (tapped) of 4.5 to 5.0 g/cc were obtained with absolute particle densities (by xylene displacement) near 10 g/cc. A single sintering test on the unground product (40- to 200-mesh particles) gave pellets with a density near 8 g/cc. Although the sintered density is low, a treatment such as ball milling or oxidation-reduction is suggested as a means of improving the sintered density for fuel elements employing pelleted uranium dioxide. The product may be well suited for dispersion or cermet type fuel elements or for future reactors employing uranium dioxide in bulk or in fused form.

An alternate application of this process is to recover the fluoride as hydrofluoric acid from the large quantities of depleted uranium hexafluoride now being stored. In this case high conversion to uranium dioxide would not be important, but a low steam excess would be desirable to produce a high assay hydrofluoric acid.

Uranium Tetrafluoride

Use of $HF-H_2O$ Azeotrope

In the past, screw reactors for the production of uranium tetrafluoride from uranium dioxide have operated with an excess of hydrogen fluoride of 2.3 times the theoretical amount. The excess reactant was condensed with the water of reaction to produce a 70 per cent hydrofluoric acid by-product. The cost of hydrogen fluoride is high enough to encourage the development of operational techniques for reducing the amount of this reagent required. To minimize reagent excesses as much as possible, the concept of recovering and recycling the 38 per cent $HF-H_2O$ azeotrope to the reactors has been investigated.[9]

Three screw reactors operate in a cascade arrangement with uranium dioxide fed to the drive end of the first reactor and anhydrous hydrogen fluoride fed to the discharge end of the last reactor. The azeotrope recycle stream is fed to the discharge end of the first reactor where it mixes with partially reacted gas flowing from the middle reactor. The off-gas leaving the first reactor is filtered, condensed, and reconcentrated to 38 per cent in a Karbate distillation column. This reconcentrated acid is then recycled, while the dilute overheads from the still are discarded.

A number of plant-scale tests were made to develop a set of conditions under which a high quality uranium tetrafluoride would be produced with the lowest possible hydrogen fluoride excess and amount of azeotrope recycle. Excellent reactor operation, comparable to the normal operation with high hydrogen fluoride excess, was obtained using an azeotrope ratio of 0.135 lb 38 per cent hydrofluoric acid per pound of uranium tetrafluoride and an over-all hydrogen fluoride rate of 1.2 times the stoichiometric amount.

Dehydration of Uranium Tetrafluoride

Uranium tetrafluoride is currently produced by a series of reactions proceeding at high temperature which result in a dry final product. Methods of producing uranium tetrafluoride from aqueous solutions have been under development at a number of sites with the object of enabling uranium mills to produce this salt as a final product, rather than the conventional uranium concentrates. Such a product, if pure, could be reduced directly to metal; if impure it could be used as feed to the new refining process based on fluorination to uranium hexafluoride.[10] The tetrafluoride produced from aqueous solution, however, contains 2.5 to 5 per cent water after drying at about 100°C. This water content must be reduced to 0.25 to 0.1 per cent for satisfactory metal production, or to some similarly low value for the hexafluoride process. Other requirements for metal production are (1) a maximum uranium dioxide content of 1.9 per cent and (2) a uranyl fluoride content between 1.0 and 2.5 per cent.

In the dehydration of uranium tetrafluoride at elevated temperatures, a difficulty arises from side reactions which occur. The released water reacts with the salt to produce uranium dioxide, and any oxygen present in the dehydration chamber can react to produce uranyl fluoride. A laboratory program has therefore been carried out in which various methods for dehydration were investigated.[11]

A minimum temperature of 400 to 500°C was found necessary for the degree of dehydra-

tion desired. Higher temperatures caused above-specification amounts of uranium dioxide. Flushing the chamber with nitrogen gas to remove water vapor also caused high uranium dioxide values, probably due to lowering of hydrogen fluoride partial pressure in the chamber. In the absence of a flush gas, sufficient hydrogen fluoride is formed in the reversible dehydration reactions to inhibit formation of an excess of uranium dioxide. The uranyl fluoride values in the product may be controlled by flushing with air for various times after steam generation is completed.

This technique of heating first with no flush and then with an air flush toward the end of the heating cycle was investigated for various sample sizes and periods of air flushing. About 200 lb of uranium tetrafluoride was dehydrated to specification material, with about 20 per cent of the salt requiring reruns to meet specifications. The marked dependence of the dehydrated salt composition on sample geometry indicates that scaling up should be thoroughly piloted to determine proper operating conditions for the larger installation.

Other workers[12] have shown that the water content of uranium tetrafluoride can be reduced to less than 0.2 per cent in an atmosphere of nitrogen with formation of less than 1.0 per cent uranium dioxide, provided that the dehydration is performed stagewise. To avoid formation of uranium dioxide, the initial dehydration temperature must be kept below approximately 350°C. As the dehydration proceeds the maximum allowable temperature increases. The pyrohydrolysis reaction was said to be catalyzed by traces of oxygen; therefore very pure nitrogen was used. A two-stage fluidized-bed dehydrator was used, the first stage being operated at 350°C and the second at 450°C. The inlet nitrogen gas was passed through a hot copper bed and a Drierite column to remove traces of oxygen and water. The uranium tetrafluoride hydrate, previously sized to between 40 and 100 mesh, was continuously fed in by a screw feeder. In general, the operation of the fluidized bed was satisfactory, but the necessity for sizing the feed was considered a disadvantage. Earlier tests with a screw-agitated heated tube failed due to poor heat transfer. No data were given on the uranyl fluoride content of the dehydrated product.

Uranium

Bomb Reduction of Uranium Tetrafluoride

As a part of an effort to improve and control uranium yields in the bomb reduction of uranium tetrafluoride with magnesium, small-scale reduction equipment is being used to perform investigations relating to production problems. The need for a better understanding of the thermal conditions in the reduction process prompted an analysis of the thermodynamics and heat transfer as applied to this process at the Fernald, Ohio, production center.[13] Preheating of the green salt–magnesium charge is stated to be necessary to bring some portion of the charge to the ignition temperature (about 900°F) and all of the charge to an average temperature (about 400°F) high enough to assure molten products. The temperature distribution in the charge as a result of preheating has been predicted as a function of the thermal properties and dimensions of the charge and of the preheat time. The temperature of the reaction products immediately after reaction has also been predicted.

After ignition, rapid propagation of the reaction is essential if a fluid product is to be formed. Reversal of the reaction at elevated temperatures is not thermodynamically possible for uranium tetrafluoride but can occur in the case of uranium dioxide or uranyl fluoride because of interaction of uranium and magnesium oxide at elevated temperatures. Solidification of the magnesium fluoride product can result from chilling effects of the liner and pot alone without loss to the surroundings. Liners of low density appear to be desirable for reducing the rate of cooling of reaction products.

Preparation of High Purity Uranium

Pure uranium is required for the determination of physical and metallurgical properties with and without small additions of alloying elements. A development program for the production of kilogram quantities of pure dendritic uranium by refinement electrolysis in fused salts has been carried out in Great Britian.[14] A 100-amp cell has been built, and experiments have been carried out to test materials of construction and to develop an operating technique. An electrolyte of lithium chloride, potassium chloride, and uranium tetrafluoride was used. A

metal recovery process was developed, and quantities of dendritic uranium powder were produced. The impurities present in magnesium-reduced metal can be largely removed, but further development is required to reduce contamination from construction materials of the electrolytic cell. The particle size of the uranium powder can be varied by altering the deposition current and operating temperature. The powders produced have been pyrophoric; material free from this disadvantage may be made by melting the powder under fused salts.

Plutonium

At the Los Alamos Scientific Laboratory, plutonium metal and plutonium solutions are analyzed for impurities by a spectrochemical method. Because of the need for plutonium dioxide suitable for use as a matrix for standards, work was undertaken to prepare a quantity of high-purity material.[15] The purification process developed consists of a partial removal of impurities by electrolysis into a mercury cathode and a subsequent further purification by precipitation of the plutonium as the peroxide. The peroxide precipitate is ignited to the dioxide at 900°C in a platinum-lined furnace under noncontaminating conditions. The product contained about 2 ppm of manganese as the only detectable metal impurity exceeding the 1 ppm level. This high quality is readily reproduced batchwise.

The preparation of a high-purity Pu(III) chloride solution is readily achieved by dissolving the above-mentioned peroxide in quartz-distilled hydrochloric acid.

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